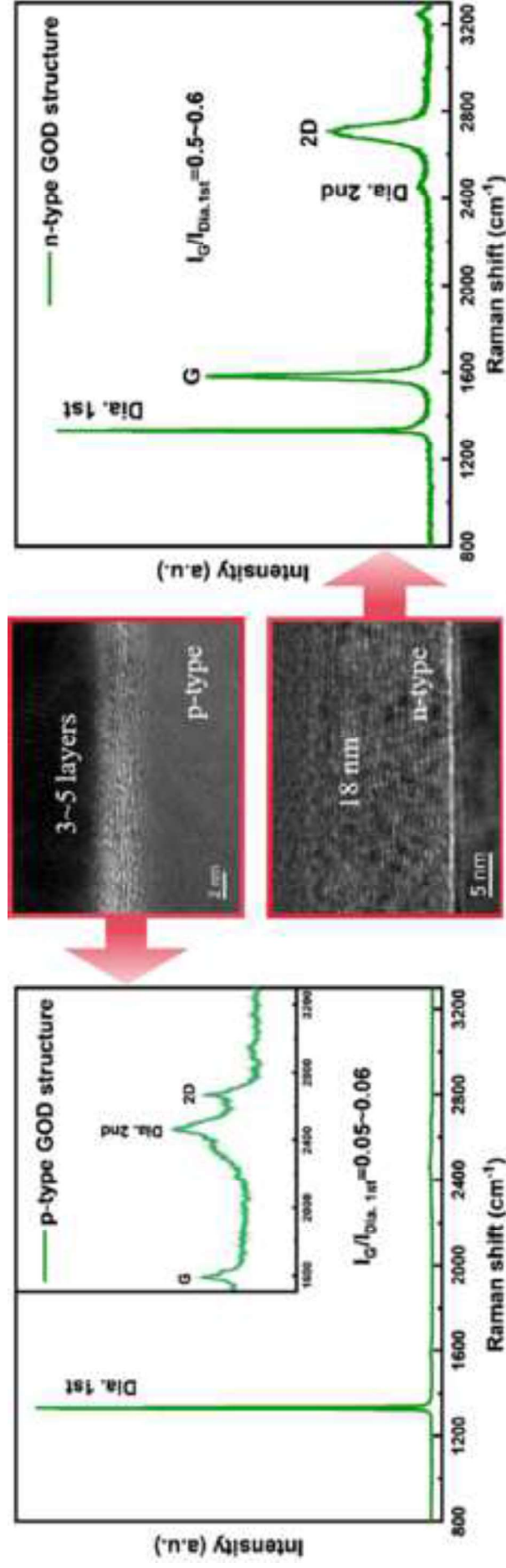




Yuan Xiaolu: Data curation, Writing-Original draft preparation. **Liu Jinlong:** Methodology. **Liu Jiangwei:** Visualization, Investigation. **Wei Junjun:** Supervision. **Chen Liangxian:** Validation. **Wang Wenrui:** Resources, Writing-Review&Editing. **Li Chengming:** Conceptualization.

Highlights

- Diverse properties of GOD structure were prepared by Ni-catalyzed after annealing.
- P-type GOD structure contains 3~5 layers graphene.
- N-type GOD structure contains multilayer graphene with lots of nickel atoms doping.



The graphene-on-diamond structure with Ni-catalyzed under high temperature

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Abstract:

Graphene-on-diamond (GOD) composite structure has been attracting considerable attention due to its unique features for all carbon sp^3 - sp^2 electronic applications. Whereby the electrical properties of diamond surface can be purposely tailored and significantly altered through transformed graphene layers. In this work, GOD composite structures were prepared by nickel (Ni)-catalyzed high-temperature rapid annealing, and were analyzed by Raman, Hall effect measurement and Transmission electron microscopy (TEM). The results show that the difference in surface conductivity of GOD composite structure is mainly related to the number of transformed graphene layers, which is mainly affected by annealing temperature, annealing time and the thickness of nickel film. Hall measurement and TEM results demonstrate that when the transformed graphene grows graphite with a lot of Ni atoms embedded into diamond, the surface carriers of GOD composite structure are electrons. On the contrary, the surface carriers are holes while the transformed graphene contains about 3 or 5 layers. These findings may provide a route for GOD structure to become a strong candidate for next generation complementary diamond electronic devices.

Keywords

Diamond; graphene; Ni; p-type; n-type

1. Introduction

Diamond and graphene exhibit excellent carrier mobility, saturation velocity, and thermal conductivity, making them both attractive materials for application in electronics of the future^[1-3]. The graphene-on-diamond (GOD) composite structure has been winning considerable attention. Naturally, lots of efforts have been done^[4-7]. One kind of GOD transistor was developed in 2012 by transferring graphene to diamond substrate^[8]. The current carrying capacity of transistor can be improved 100 times than on Si substrate, which is hopeful in interconnects and high-power devices application^[9-11]. Additionally, the graphite(graphene)-diamond hybrid structure makes it possible to turn insulating diamond into superconductor^[12]. Therefore, the GOD structure maybe leads to the new sp^3 - sp^2 carbon technology.

In general, diamond itself will be graphitized at high temperature and directly transformed into graphene structure^[13]. The introduction of catalyst may reduce the phase transition temperature^[14]. And the number of graphene layers can be regulated by adjusting the annealing conditions^[15,16]. Interestingly, diverse surface carrier concentration and mobility of GOD structures are produced under different annealing conditions^[17-19]. In 2016, Ueda et al of Nagoya University prepared the GOD structure by annealing of Cu/diamond heterostructures at 950 °C for 90 min. The sheet hole concentration and mobility values of the layers were estimated to be $\sim 10^{13} \text{ cm}^{-2}$ and $\sim 410 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Furthermore, the mobility approaches to as high as $670 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 50 K. Later, Kanada et al annealed single crystal diamond at 900 °C for 1 min using nickel as catalyst, and obtained a mixed graphene layer with certain monolayer coverage. Hall measurement reveals that the GOD structure is also p-type, and the sheet concentration and mobility at room temperature are $5.7 \times 10^{13} \text{ cm}^{-2}$ and $140 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Recently, a mixture of graphene layer was grown directly on (100) single-crystalline diamond using Ni as catalyst at 800 °C for 1min. The hole mobility was calculated to be around $79 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $123 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature and at 80 K, respectively.

However, the surface carriers of GOD structure in most previous work of researchers are holes, that is, p-type. Recently, Liu et al of Jilin University obtained

successfully the n-type GOD structure with high mobility of $737\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature directly by regulating the annealing and cooling temperature^[20]. More intriguing features would come from this kind of in-situ GOD structure. In this paper, the formation of high-quality graphene layers on diamond was achieved based on high-temperature annealing using a Ni catalyst. Two varieties of GOD structure carriers emerged in response to varying annealing conditions. And their surface conductivities and interface topologies of GOD were both analyzed.

2. Methodology

2.1 Preparation of GOD structure

The GOD structure was prepared by Ni-catalyzed diamond after fast annealing using direct current (DC) arc jet plasma equipment, as shown in Figure 1a. Compared to the normal rapid thermal annealing furnace, the DC arc jet plasma furnace has an extremely fast heating rate ($>10\text{ }^\circ\text{C/s}$) and a relatively high vacuum ($<1\text{ Pa}$). The annealing process is completed instantaneously when the DC arc plasma is generated, contributing to the accurate control of annealing time, which is helpful to obtain few-layer graphene, not multilayer graphite. And the annealing temperature could be modulated by the arc power. A detailed schematic diagram of GOD preparation process is displayed in Figure 1b. Firstly, several (100) orientation single crystal diamond substrates were polished and cleaned by mixed acid ($\text{H}_2\text{SO}_4:\text{HNO}_3=1:3$). The surface roughness of R_a was below 1 nm ($20\text{ }\mu\text{m}\times 20\text{ }\mu\text{m}$) for all diamond samples^[21]. Secondly, the metal catalysts were deposited on the surface of diamond substrates by magnetron sputtering. The range of thickness for Ni films was set to $10\sim 100\text{ nm}$. Upon incrementing the film's thickness, the catalytic Ni undergoes a phase transition from an amorphous to a crystalline state, as demonstrated in Figure S1 (see Supplementary). Then, the nickel-coated single crystal diamond samples were annealed under mixed Ar_2/H_2 atmosphere. After rapid annealing, the nickel-coated single crystal diamond samples were immersed in diluted acid (hydrochloric acid or nitric acid) until the remaining Ni was completely dissolved.

2.2 Characterization of GOD structure

The Vander Paul method was used to measure the surface conductivity of the GOD

structure at room temperature using an Ecopia HMS-3000 instrument. Four gold electrodes were deposited on the edge of GOD structure surface by photolithography (Figure 1c). The applied magnetic field strength is 0.5 T. And the test current is set to in the range of nA to mA. The results obtained in the tables are the average values of 3 samples taken under the same environment after 3 measurements for each sample. A preliminary detection of the graphene structure on the diamond substrate was made by Raman spectroscopy (Instrument: Renishaw inVia Qontor). The laser wavelength is 532 nm. The chemical states of C, O, Ni elements on GOD surface are characterized by X ray photoelectron spectroscopy (XPS) (Instrument: ESCALAB Xi⁺). TEM (Instrument: JEM-ARM300F) is used to observe the number of graphene layers and the interface between graphene and diamond. Electron energy loss spectroscopy (EELS) is applied to analyze the hybrid state of carbon atoms between diamond and graphene.

3. Results and Discussion

Two types of carriers of GOD structure were generated by regulating the Ni thickness and annealing temperature, as described in table 1 and table 2. When the thickness of deposited Ni is too thin (10 nm), the surface conductivity of GOD cannot be measured due to the discontinuous graphene structure. Which is caused by the nickel layer agglomerating at high temperature to produce particles^[22]. As the thickness of nickel film increases to 15 nm and 25 nm, the graphene on diamond surface grows continuous but thin. The surface carriers of GOD structure are measured as holes (p-type) with around $10^4 \text{ } \Omega/\square$ of surface sheet resistance and 10^{13} cm^{-2} of sheet concentration. As the thickness of the nickel film increases to 50 nm and 100 nm, the quantity of graphene layers on the diamond surface progressively boosts. The surface carrier of GOD becomes electron (n-type), following the surface sheet resistance decreases to $1.0 \text{ } \Omega/\square$. The concentration of surface carrier naturally rises to $\sim 10^{16} \text{ cm}^{-2}$. It is worth mentioning that the Hall mobilities of all samples are less than $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Hall measurement results of GOD structure are obtained at three levels of temperature (Table 2). The hole carriers of GOD structure with around a 10^{14} cm^{-2}

concentration are present after the 800 °C annealing. The Hall mobility exceeds 100 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and the sheet resistance is approximately $10^2 \Omega/\square$. As the temperature reaches to 1000 °C, the surface carriers of GOD structure become electrons (n-type). In addition, it reveals metal conductivity properties^[23], showing a decrease in surface sheet resistance to $1.2 \Omega/\square$ and an increase in surface carrier concentration to approximately 10^{16} cm^{-2} . Further, the Hall mobility exceeds $300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Strangely, it is impossible to identify the kind of surface carrier of the GOD structure after annealing at 900 °C. Its surface carrier concentration is $\sim 10^{14} \text{ cm}^{-2}$, and the Hall mobility is relatively low, only $15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. One possible explanation is that the surface structure of graphene suffers damage during the removal of residual nickel^[24].

Annealing time is another crucial annealing parameter for GOD structure. Table 3 illustrates the effect of annealing time on the surface conductivity of GOD structure with 40 nm Ni film at 800 °C. All of samples are p-type conductivities and the surface mobilities are less than $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The findings suggest prolonging the annealing time has little effect on surface conductivity, especially for the improvement of mobility, provided that a specific thickness of nickel film and annealing temperature are achieved. However, the surface mobility of the GOD structure appears to be significantly influenced by the varieties of diamond substrate (Figure S2). Higher Hall mobility of $380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was measured on Chemical Vapor Deposition (CVD) diamond substrate (see Table 4), though the surface conductivity of three types of samples is p-type. The probably reason could be the transport of surface hole carriers is more impacted by isolated nitrogen defects in high temperature high pressure (HTHP) samples than by nitrogen vacancy defects in CVD samples^[25].

Figure 2 shows the typical Raman spectrum of two kinds of GOD structure. Peak Dia.1st ($\sim 1332 \text{ cm}^{-1}$) and peak Dia.2st ($\sim 2450 \text{ cm}^{-1}$) represent the $\text{sp}^3\text{-C}$ structure of diamond, respectively. Peak G ($\sim 1580 \text{ cm}^{-1}$) and peak 2D ($\sim 2700 \text{ cm}^{-1}$) represent the $\text{sp}^2\text{-C}$ structure of graphene, respectively. Particularly, the conventional separation principle of Raman peak is no longer valid for the GOD structure due to the influence of diamond substrate^[26]. Instead, the intensity ratio of peak G to peak Dia.1st was used to distinguish the graphene layers of GOD structure. In all p-type GOD samples, the

intensity ratio of peak G to peak Dia.1st is about 0.05~0.06 (Figure 2a). which only qualitatively indicate that there are few layers of graphene on diamond substrate. Inversely, typical features of graphene were observed in Figure 2b^[27]. More sp^2 carbon on the diamond substrate corresponds to a greater intensity. That is, the n-type GOD structure includes more transformed graphene layers. In all n-type GOD samples, the intensity ratio of peak G to peak Dia.1st is around 0.5~0.6. The absence of D peak (1350 cm^{-1}) representing defect in the Raman spectra indicates the diamond surface produced high-quality graphene^[28].

Three elements (Si C O) are detected at the surface of p-type GOD structure as shown in XPS spectrums (Figure 3). Calibrated by the binding energy of Si (102 eV), the binding energy of C-C bond on the surface of GOD sample is 284.4 eV^[29]. The binding energy of O element in Si-O bond is 532.1 eV. As per semi-quantitative analysis, the atoms of C are the most. The atomic specific contents of C, Si, O, Ni are 73.18%, 8.78%, 17.44% and 0.60%, respectively. It contains the impurities Si and O, and barely no Ni element is found. On the contrary, obvious Ni2p peaks present on the surface of n-type GOD structure as described in Figure 4. The atoms of Ni are nearly 5%. After fitting the peaks of C1s, O1s and Ni2p_{3/2}, a small amount of nickel oxide is detected at the surface of n-type GOD structure^[30]. Apparently, it can be inferred that the n-type GOD structure is not only connected to the number of graphene layers, but also affected by the Ni doping.

To understand deeply its interface structure and figure out the specific layers of graphene, HR (High Resolution) TEM observation and EELS analysis were applied. Figure 5 displays the TEM images and EELS spectrums of p-type GOD structure. 3 or 5 layers of graphene are transformed from diamond (Figure 5b). Furthermore, the sp^3 - sp^2 hybrid bonding was found at the interface of graphene and diamond (Figure 5c). EELS Line scan spectrum also prove it. 8 points at the interface (Figure 5a) were picked to compare the differences of diamond and graphene. Ti elements discovered in Figure 5d were attributed to the protective layer deposited on the surface of GOD sample before TEM observation. In the low energy loss region (Figure 5e), the plasma peak of diamond moves to the direction of low energy electron loss. The width of bandgap

changes from 5.50 eV to 4.75 eV^[31,32]. In the high energy loss region (Figure 5f), a strong σ^* peak (285.3 eV) has been identified at near the diamond region, showing distinct sp^3 hybrid characteristics^[33]. When the measurement region approaches graphene, the σ^* peak signal declines gradually, and the π^* peak (284.8 eV) representing the sp^2 hybrid bond appears. The σ^* peak signal and π^* peak signal were detected simultaneously in the spectral line between intrinsic diamond and graphene region.

For n-type GOD structure (Figure 6), multilayer graphene (or graphite) emerges on diamond surface. The thickness of graphene is measured to approximately 18 nm. A lot of Ni atoms embedded in diamond substrate, which is agreement to XPS observations. In the low energy loss region, the plasma peak of diamond still shifts into low loss region. While in the high energy loss region, a more complex bonding state exists in Figure 6g, probably owing to the nickel-carbide inside the diamond. Considering that the transport carriers of metal and graphite are both electrons, the surface conductivity of GOD structure measured by Hall is a mixed structure of nickel-carbide and graphite. Therefore, the main reason for n-type GOD structure is directly attributed to nickel doping in the multilayer graphene (graphite). In contrast, p-type GOD structures have few-layered graphene with clear interfaces and do not contain nickel doping, which has been proved by XPS, TEM and EELS. Nevertheless, the fundamental mechanisms of carrier transport on GOD structure are still unclear and need to be further studied. A band diagram of two kinds of GOD structure might be established to explain it.

4. Conclusion

The GOD structure can be fabricated after fast annealing with Ni-catalyzed using DC arc jet plasma equipment. The catalyst thickness and annealing temperature are the key factors, followed by the annealing time and diamond substrate. The surface conductivity of GOD structure is mainly related to the number of layers of transformed graphene. As the layers of transformed graphene on diamond is about 3~5 layers, the surface carriers of GOD structure are holes (p-type). When the transformed graphene

layers develop into graphite, embedded with a lot of Ni atoms, the surface carriers of GOD structure are electrons (n-type). These findings may provide a route for GOD structure to become a strong candidate for next generation complementary diamond electronic devices.

Figures and tables

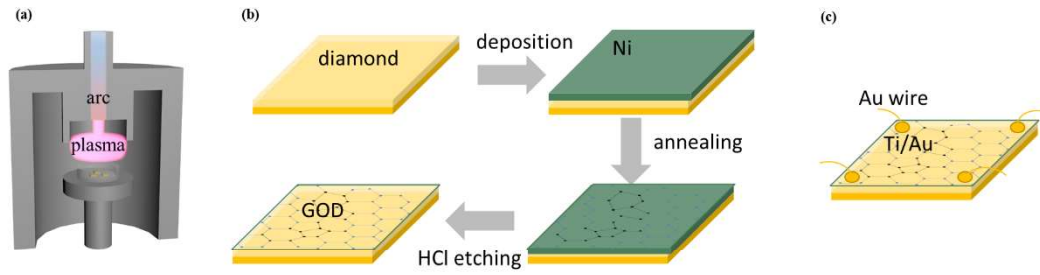


Figure 1

Table 1

Ni thickness (nm)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
10	$\sim 10^8$	--	--	--
15	$\sim 10^4$	$\sim 10^{13}$	29	p
25	$\sim 10^4$	$\sim 10^{13}$	19	p
50	1.0	$\sim 10^{16}$	84	n
100	1.0	$\sim 10^{16}$	67	n

Table 2

Temperature ($^{\circ}\text{C}$)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
800	$\sim 10^2$	$\sim 10^{14}$	114	p
900	$\sim 10^3$	$\sim 10^{14}$	15	n/p
1000	1.2	$\sim 10^{16}$	345	n

Table 3

Time (min)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
1.0	$\sim 10^4$	$\sim 10^{12}$	37	p
1.5	$\sim 10^3$	$\sim 10^{13}$	33	p
2.0	$\sim 10^3$	$\sim 10^{12}$	53	p
2.5	$\sim 10^2$	$\sim 10^{14}$	55	p
3.0	$\sim 10^3$	$\sim 10^{13}$	82	p

Table 4

Diamond substrate	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
HTHP Diamond	$\sim 10^4$	$\sim 10^{13}$	37	p
CVD Diamond	$\sim 10^4$	$\sim 10^{11}$	380	p
Epitaxial Diamond	$\sim 10^4$	$\sim 10^{12}$	154	p

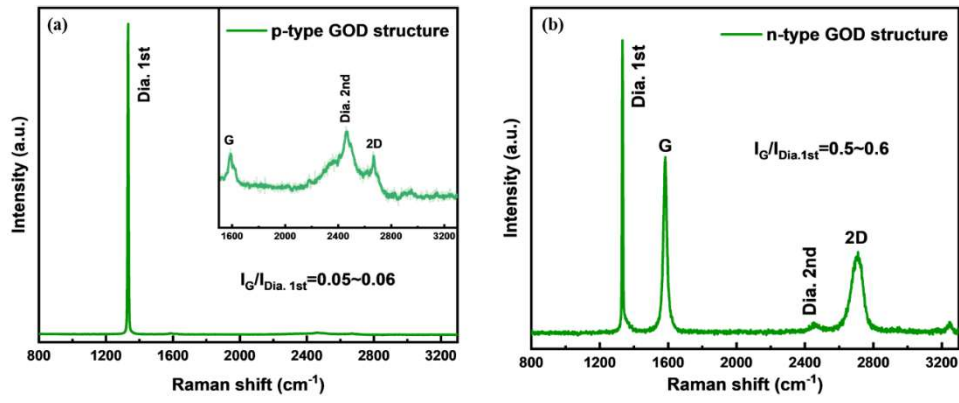


Figure 2

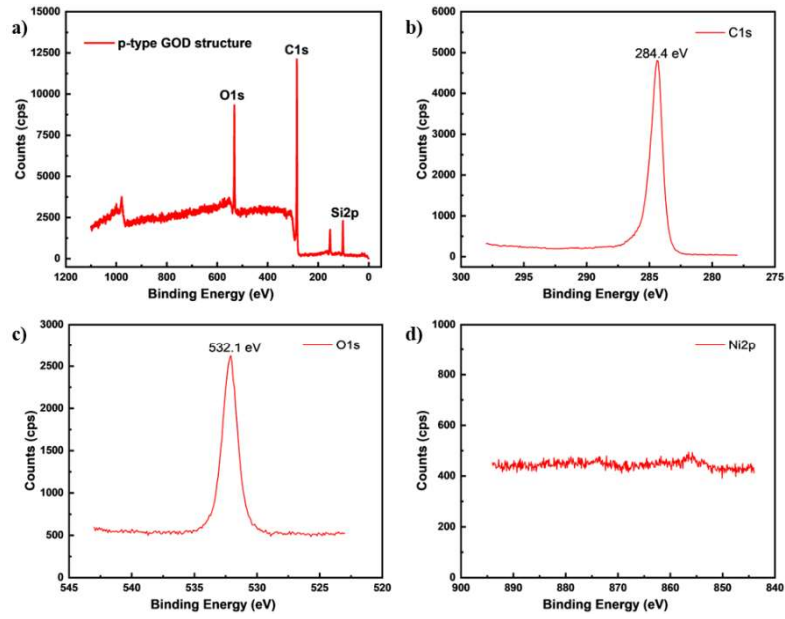


Figure 3

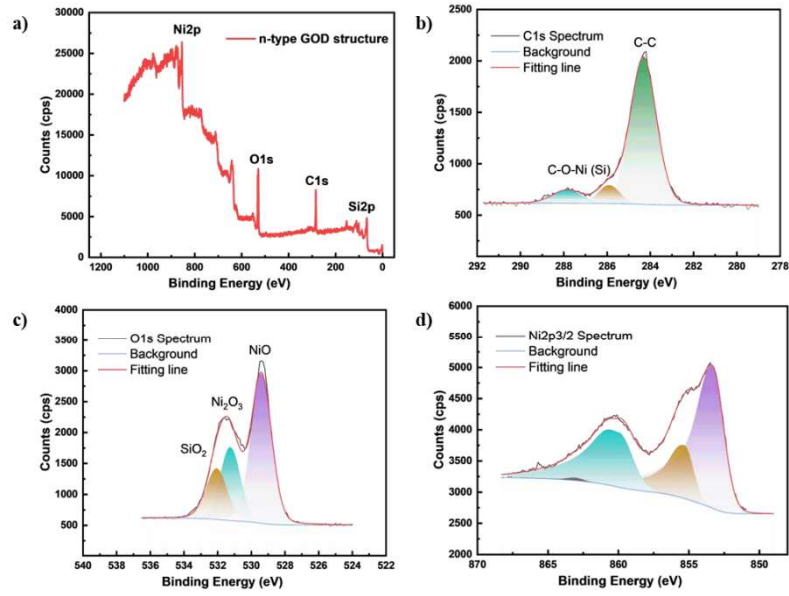


Figure 4

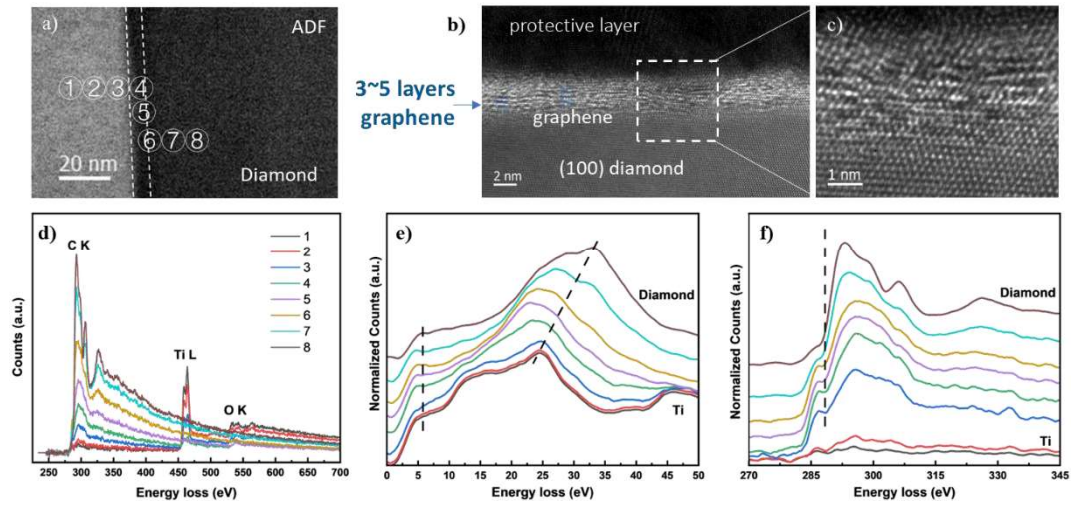


Figure 5

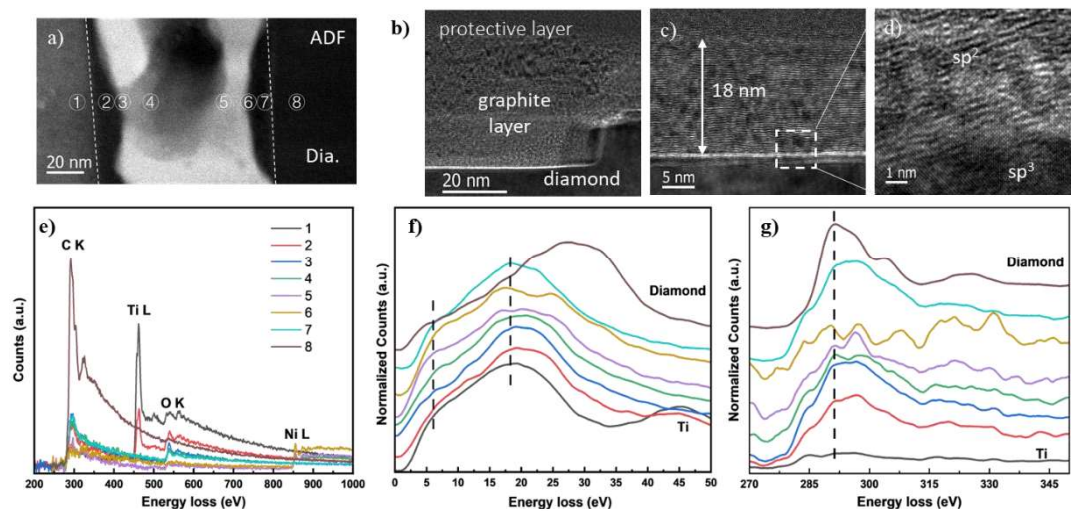


Figure 6

Captions:

Figure 1 Schematic diagram of GOD structure fabrication. (a) DC arc jet plasma equipment (b) Flow chart (c) Hall measurement using Van der Paw method.

Table 1 Hall measurements of GOD structure with different Ni thickness under 800 °C for 1.5 min.

Table 2 Hall measurements of GOD structure under different annealing temperature with 40 nm Ni film for 1.5 min.

Table 3 Hall measurements of GOD structure under different annealing time with 40 nm Ni film at 800 °C.

Table 4 Hall measurements of GOD structure under different diamond substrate with 40 nm Ni film at 800 °C for 1.5 min.

Figure 2 Raman spectrum of GOD structure. (a) p-type (b) n-type. I_G means the Intensity of G peak of graphene. $I_{\text{Dia.1st}}$ means the Intensity of first-order peak of diamond. Dia.2nd means the second-order peak of diamond.

Figure 3 XPS Spectrum of p-type GOD structure. (a) Survey (b) C1s (c) O1s (d) Ni2p

Figure 4 XPS Spectrum of n-type GOD structure. (a) Survey (b) C1s (c) O1s (d) Ni2p_{3/2}

Figure 5 TEM images and EELS spectrums of p-type GOD structure. (a) ADF image for line scan (b) HRTEM image (c) Zoom-in area (d) EELS line scan spectrum (e) Low loss of C K edge (f) High loss of C K edge

Figure 6 TEM images and EELS spectrums of n-type GOD structure. (a) ADF image for line scan (b) and (c) HRTEM images (d) Zoom-in area (e) EELS line scan spectrum (f) Low loss of C K edge (g) High loss of C K edge

CRedit author statement

Yuan Xiaolu: Data curation, Writing-Original draft preparation. **Liu Jinlong:** Methodology. **Liu Jiangwei:** Visualization, Investigation. **Wei Junjun:** Supervision. **Chen Liangxian:** Validation. **Wang Wenrui:** Resources, Writing-Review&Editing. **Li Chengming:** Conceptualization.

Acknowledgement

This work was supported by the National High-level University-sponsored Graduate Program of China Scholarship Council (CSC).

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The graphene-on-diamond structure with Ni-catalyzed under high temperature

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Abstract:

Graphene-on-diamond (GOD) composite structure has been attracting considerable attention due to its unique features for all carbon sp^3 - sp^2 electronic applications. Whereby the electrical properties of diamond surface can be purposely tailored and significantly altered through transformed graphene layers. In this work, GOD composite structures were prepared by nickel (Ni)-catalyzed high-temperature rapid annealing, and were analyzed by Raman, Hall effect measurement and Transmission electron microscopy (TEM). The results show that the difference in surface conductivity of GOD composite structure is mainly related to the number of transformed graphene layers, which is mainly affected by annealing temperature, annealing time and the thickness of nickel film. Hall measurement and TEM results demonstrate that when the transformed graphene grows graphite with a lot of Ni atoms embedded into diamond, the surface carriers of GOD composite structure are electrons. On the contrary, the surface carriers are holes while the transformed graphene contains about 3 or 5 layers. These findings may provide a route for GOD structure to become a strong candidate for next generation complementary diamond electronic devices.

Keywords

Diamond; graphene; Ni; p-type; n-type

1. Introduction

Diamond and graphene exhibit excellent carrier mobility, saturation velocity, and thermal conductivity, making them both attractive materials for application in electronics of the future^[1-3]. The graphene-on-diamond (GOD) composite structure has been winning considerable attention. Naturally, lots of efforts have been done^[4-7]. One kind of GOD transistor was developed in 2012 by transferring graphene to diamond substrate^[8]. The current carrying capacity of transistor can be improved 100 times than on Si substrate, which is hopeful in interconnects and high-power devices application^[9-11]. Additionally, the graphite(graphene)-diamond hybrid structure makes it possible to turn insulating diamond into superconductor^[12]. Therefore, the GOD structure maybe leads to the new sp^3 - sp^2 carbon technology.

In general, diamond itself will be graphitized at high temperature and directly transformed into graphene structure^[13]. The introduction of catalyst may reduce the phase transition temperature^[14]. And the number of graphene layers can be regulated by adjusting the annealing conditions^[15,16]. Interestingly, diverse surface carrier concentration and mobility of GOD structures are produced under different annealing conditions^[17-19]. In 2016, Ueda et al of Nagoya University prepared the GOD structure by annealing of Cu/diamond heterostructures at 950 °C for 90 min. The sheet hole concentration and mobility values of the layers were estimated to be $\sim 10^{13} \text{ cm}^{-2}$ and $\sim 410 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Furthermore, the mobility approaches to as high as $670 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 50 K. Later, Kanada et al annealed single crystal diamond at 900 °C for 1 min using nickel as catalyst, and obtained a mixed graphene layer with certain monolayer coverage. Hall measurement reveals that the GOD structure is also p-type, and the sheet concentration and mobility at room temperature are $5.7 \times 10^{13} \text{ cm}^{-2}$ and $140 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Recently, a mixture of graphene layer was grown directly on (100) single-crystalline diamond using Ni as catalyst at 800 °C for 1min. The hole mobility was calculated to be around $79 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $123 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature and at 80 K, respectively.

However, the surface carriers of GOD structure in most previous work of researchers are holes, that is, p-type. Recently, Liu et al of Jilin University obtained

successfully the n-type GOD structure with high mobility of $737\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature directly by regulating the annealing and cooling temperature^[20]. More intriguing features would come from this kind of in-situ GOD structure. In this paper, the formation of high-quality graphene layers on diamond was achieved based on high-temperature annealing using a Ni catalyst. Two varieties of GOD structure carriers emerged in response to varying annealing conditions. And their surface conductivities and interface topologies of GOD were both analyzed.

2. Methodology

2.1 Preparation of GOD structure

The GOD structure was prepared by Ni-catalyzed diamond after fast annealing using direct current (DC) arc jet plasma equipment, as shown in Figure 1a. Compared to the normal rapid thermal annealing furnace, the DC arc jet plasma furnace has an extremely fast heating rate ($>10\text{ }^\circ\text{C/s}$) and a relatively high vacuum ($<1\text{ Pa}$). The annealing process is completed instantaneously when the DC arc plasma is generated, contributing to the accurate control of annealing time, which is helpful to obtain few-layer graphene, not multilayer graphite. And the annealing temperature could be modulated by the arc power. A detailed schematic diagram of GOD preparation process is displayed in Figure 1b. Firstly, several (100) orientation single crystal diamond substrates were polished and cleaned by mixed acid ($\text{H}_2\text{SO}_4:\text{HNO}_3=1:3$). The surface roughness of R_a was below 1 nm ($20\text{ }\mu\text{m}\times 20\text{ }\mu\text{m}$) for all diamond samples^[21]. Secondly, the metal catalysts were deposited on the surface of diamond substrates by magnetron sputtering. The range of thickness for Ni films was set to $10\sim 100\text{ nm}$. Upon incrementing the film's thickness, the catalytic Ni undergoes a phase transition from an amorphous to a crystalline state, as demonstrated in Figure S1 (see Supplementary). Then, the nickel-coated single crystal diamond samples were annealed under mixed Ar_2/H_2 atmosphere. After rapid annealing, the nickel-coated single crystal diamond samples were immersed in diluted acid (hydrochloric acid or nitric acid) until the remaining Ni was completely dissolved.

2.2 Characterization of GOD structure

The Vander Paul method was used to measure the surface conductivity of the GOD

structure at room temperature using an Ecopia HMS-3000 instrument. Four gold electrodes were deposited on the edge of GOD structure surface by photolithography (Figure 1c). The applied magnetic field strength is 0.5 T. And the test current is set to in the range of nA to mA. The results obtained in the tables are the average values of 3 samples taken under the same environment after 3 measurements for each sample. A preliminary detection of the graphene structure on the diamond substrate was made by Raman spectroscopy (Instrument: Renishaw inVia Qontor). The laser wavelength is 532 nm. The chemical states of C, O, Ni elements on GOD surface are characterized by X ray photoelectron spectroscopy (XPS) (Instrument: ESCALAB Xi⁺). TEM (Instrument: JEM-ARM300F) is used to observe the number of graphene layers and the interface between graphene and diamond. Electron energy loss spectroscopy (EELS) is applied to analyze the hybrid state of carbon atoms between diamond and graphene.

3. Results and Discussion

Two types of carriers of GOD structure were generated by regulating the Ni thickness and annealing temperature, as described in table 1 and table 2. When the thickness of deposited Ni is too thin (10 nm), the surface conductivity of GOD cannot be measured due to the discontinuous graphene structure. Which is caused by the nickel layer agglomerating at high temperature to produce particles^[22]. As the thickness of nickel film increases to 15 nm and 25 nm, the graphene on diamond surface grows continuous but thin. The surface carriers of GOD structure are measured as holes (p-type) with around $10^4 \text{ } \Omega/\square$ of surface sheet resistance and 10^{13} cm^{-2} of sheet concentration. As the thickness of the nickel film increases to 50 nm and 100 nm, the quantity of graphene layers on the diamond surface progressively boosts. The surface carrier of GOD becomes electron (n-type), following the surface sheet resistance decreases to $1.0 \text{ } \Omega/\square$. The concentration of surface carrier naturally rises to $\sim 10^{16} \text{ cm}^{-2}$. It is worth mentioning that the Hall mobilities of all samples are less than $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Hall measurement results of GOD structure are obtained at three levels of temperature (Table 2). The hole carriers of GOD structure with around a 10^{14} cm^{-2}

concentration are present after the 800 °C annealing. The Hall mobility exceeds 100 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and the sheet resistance is approximately $10^2 \Omega/\square$. As the temperature reaches to 1000 °C, the surface carriers of GOD structure become electrons (n-type). In addition, it reveals metal conductivity properties^[23], showing a decrease in surface sheet resistance to $1.2 \Omega/\square$ and an increase in surface carrier concentration to approximately 10^{16} cm^{-2} . Further, the Hall mobility exceeds $300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Strangely, it is impossible to identify the kind of surface carrier of the GOD structure after annealing at 900 °C. Its surface carrier concentration is $\sim 10^{14} \text{ cm}^{-2}$, and the Hall mobility is relatively low, only $15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. One possible explanation is that the surface structure of graphene suffers damage during the removal of residual nickel^[24].

Annealing time is another crucial annealing parameter for GOD structure. Table 3 illustrates the effect of annealing time on the surface conductivity of GOD structure with 40 nm Ni film at 800 °C. All of samples are p-type conductivities and the surface mobilities are less than $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The findings suggest prolonging the annealing time has little effect on surface conductivity, especially for the improvement of mobility, provided that a specific thickness of nickel film and annealing temperature are achieved. However, the surface mobility of the GOD structure appears to be significantly influenced by the varieties of diamond substrate (Figure S2). Higher Hall mobility of $380 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was measured on Chemical Vapor Deposition (CVD) diamond substrate (see Table 4), though the surface conductivity of three types of samples is p-type. The probably reason could be the transport of surface hole carriers is more impacted by isolated nitrogen defects in high temperature high pressure (HTHP) samples than by nitrogen vacancy defects in CVD samples^[25].

Figure 2 shows the typical Raman spectrum of two kinds of GOD structure. Peak Dia.1st ($\sim 1332 \text{ cm}^{-1}$) and peak Dia.2st ($\sim 2450 \text{ cm}^{-1}$) represent the $\text{sp}^3\text{-C}$ structure of diamond, respectively. Peak G ($\sim 1580 \text{ cm}^{-1}$) and peak 2D ($\sim 2700 \text{ cm}^{-1}$) represent the $\text{sp}^2\text{-C}$ structure of graphene, respectively. Particularly, the conventional separation principle of Raman peak is no longer valid for the GOD structure due to the influence of diamond substrate^[26]. Instead, the intensity ratio of peak G to peak Dia.1st was used to distinguish the graphene layers of GOD structure. In all p-type GOD samples, the

intensity ratio of peak G to peak Dia.1st is about 0.05~0.06 (Figure 2a). which only qualitatively indicate that there are few layers of graphene on diamond substrate. Inversely, typical features of graphene were observed in Figure 2b^[27]. More sp² carbon on the diamond substrate corresponds to a greater intensity. That is, the n-type GOD structure includes more transformed graphene layers. In all n-type GOD samples, the intensity ratio of peak G to peak Dia.1st is around 0.5~0.6. The absence of D peak (1350 cm⁻¹) representing defect in the Raman spectra indicates the diamond surface produced high-quality graphene^[28].

Three elements (Si C O) are detected at the surface of p-type GOD structure as shown in XPS spectrums (Figure 3). Calibrated by the binding energy of Si (102 eV), the binding energy of C-C bond on the surface of GOD sample is 284.4 eV^[29]. The binding energy of O element in Si-O bond is 532.1 eV. As per semi-quantitative analysis, the atoms of C are the most. The atomic specific contents of C, Si, O, Ni are 73.18%, 8.78%, 17.44% and 0.60%, respectively. It contains the impurities Si and O, and barely no Ni element is found. On the contrary, obvious Ni2p peaks present on the surface of n-type GOD structure as described in Figure 4. The atoms of Ni are nearly 5%. After fitting the peaks of C1s, O1s and Ni2p3/2, a small amount of nickel oxide is detected at the surface of n-type GOD structure^[30]. Apparently, it can be inferred that the n-type GOD structure is not only connected to the number of graphene layers, but also affected by the Ni doping.

To understand deeply its interface structure and figure out the specific layers of graphene, HR (High Resolution) TEM observation and EELS analysis were applied. Figure 5 displays the TEM images and EELS spectrums of p-type GOD structure. 3 or 5 layers of graphene are transformed from diamond (Figure 5b). Furthermore, the sp³-sp² hybrid bonding was found at the interface of graphene and diamond (Figure 5c). EELS Line scan spectrum also prove it. 8 points at the interface (Figure 5a) were picked to compare the differences of diamond and graphene. Ti elements discovered in Figure 5d were attributed to the protective layer deposited on the surface of GOD sample before TEM observation. In the low energy loss region (Figure 5e), the plasma peak of diamond moves to the direction of low energy electron loss. The width of bandgap

changes from 5.50 eV to 4.75 eV^[31,32]. In the high energy loss region (Figure 5f), a strong σ^* peak (285.3 eV) has been identified at near the diamond region, showing distinct sp^3 hybrid characteristics^[33]. When the measurement region approaches graphene, the σ^* peak signal declines gradually, and the π^* peak (284.8 eV) representing the sp^2 hybrid bond appears. The σ^* peak signal and π^* peak signal were detected simultaneously in the spectral line between intrinsic diamond and graphene region.

For n-type GOD structure (Figure 6), multilayer graphene (or graphite) emerges on diamond surface. The thickness of graphene is measured to approximately 18 nm. A lot of Ni atoms embedded in diamond substrate, which is agreement to XPS observations. In the low energy loss region, the plasma peak of diamond still shifts into low loss region. While in the high energy loss region, a more complex bonding state exists in Figure 6g, probably owing to the nickel-carbide inside the diamond.

Considering that the transport carriers of metal and graphite are both electrons, the surface conductivity of GOD structure measured by Hall is a mixed structure of nickel-carbide and graphite. Therefore, the main reason for n-type GOD structure is directly attributed to nickel doping in the multilayer graphene (graphite). In contrast, p-type GOD structures have few-layered graphene with clear interfaces and do not contain nickel doping, which has been proved by XPS, TEM and EELS. Nevertheless, the fundamental mechanisms of carrier transport on GOD structure are still unclear and need to be further studied. A band diagram of two kinds of GOD structure might be established to explain it.

4. Conclusion

The GOD structure can be fabricated after fast annealing with Ni-catalyzed using DC arc jet plasma equipment. The catalyst thickness and annealing temperature are the key factors, followed by the annealing time and diamond substrate. The surface conductivity of GOD structure is mainly related to the number of layers of transformed graphene. As the layers of transformed graphene on diamond is about 3~5 layers, the surface carriers of GOD structure are holes (p-type). When the transformed graphene

layers develop into graphite, embedded with a lot of Ni atoms, the surface carriers of GOD structure are electrons (n-type). These findings may provide a route for GOD structure to become a strong candidate for next generation complementary diamond electronic devices.

Figures and tables

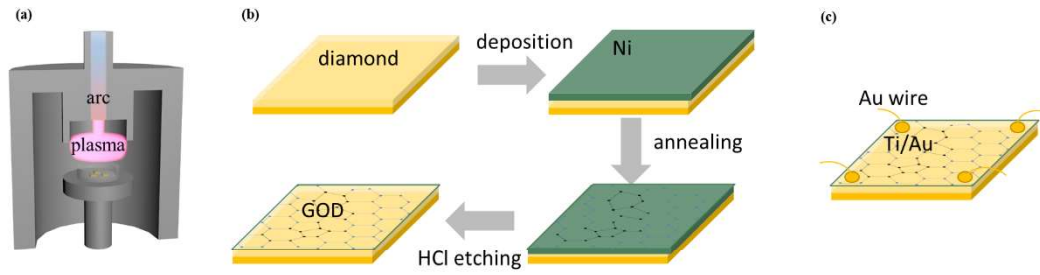


Figure 1

Table 1

Ni thickness (nm)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
10	$\sim 10^8$	--	--	--
15	$\sim 10^4$	$\sim 10^{13}$	29	p
25	$\sim 10^4$	$\sim 10^{13}$	19	p
50	1.0	$\sim 10^{16}$	84	n
100	1.0	$\sim 10^{16}$	67	n

Table 2

Temperature ($^{\circ}\text{C}$)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
800	$\sim 10^2$	$\sim 10^{14}$	114	p
900	$\sim 10^3$	$\sim 10^{14}$	15	n/p
1000	1.2	$\sim 10^{16}$	345	n

Table 3

Time (min)	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
1.0	$\sim 10^4$	$\sim 10^{12}$	37	p
1.5	$\sim 10^3$	$\sim 10^{13}$	33	p
2.0	$\sim 10^3$	$\sim 10^{12}$	53	p
2.5	$\sim 10^2$	$\sim 10^{14}$	55	p
3.0	$\sim 10^3$	$\sim 10^{13}$	82	p

Table 4

Diamond substrate	Sheet resistance ($\Omega/\square$)	Sheet concentration (cm^{-2})	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Conductivity type
HTHP Diamond	$\sim 10^4$	$\sim 10^{13}$	37	p
CVD Diamond	$\sim 10^4$	$\sim 10^{11}$	380	p
Epitaxial Diamond	$\sim 10^4$	$\sim 10^{12}$	154	p

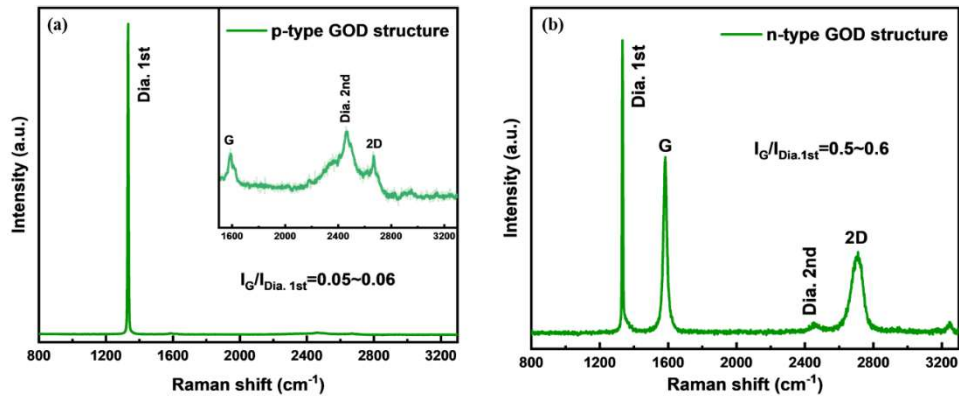


Figure 2

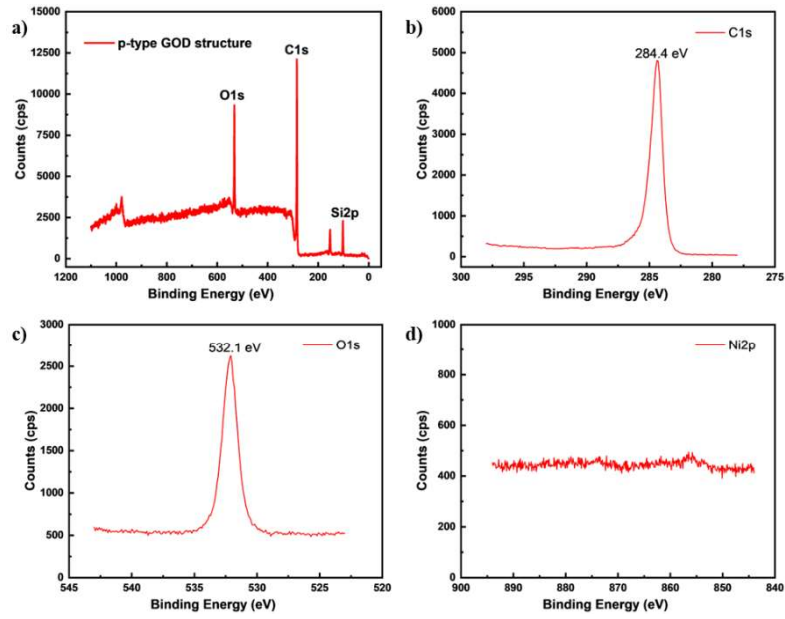


Figure 3

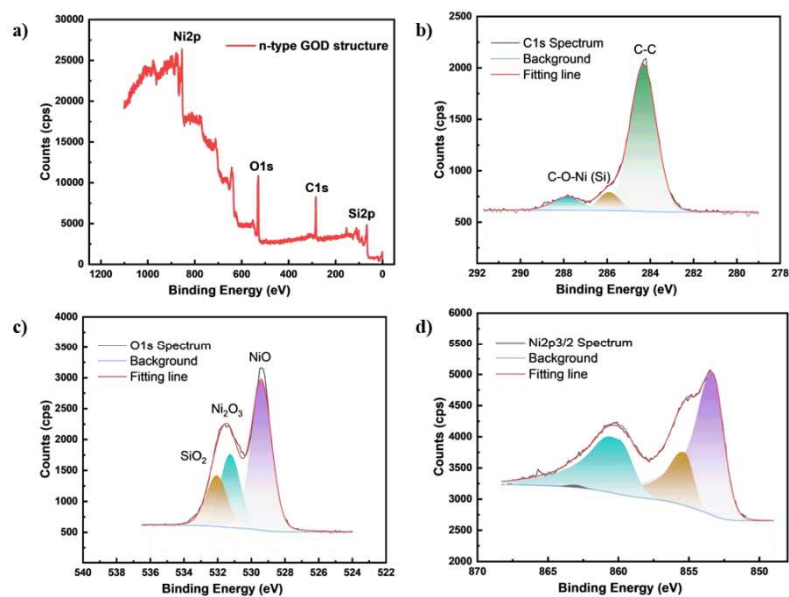


Figure 4

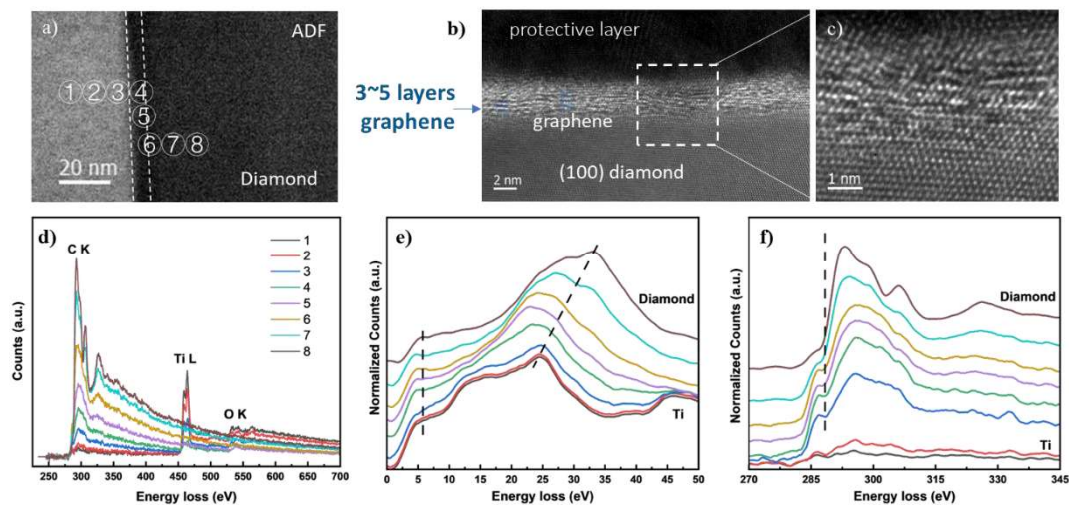


Figure 5

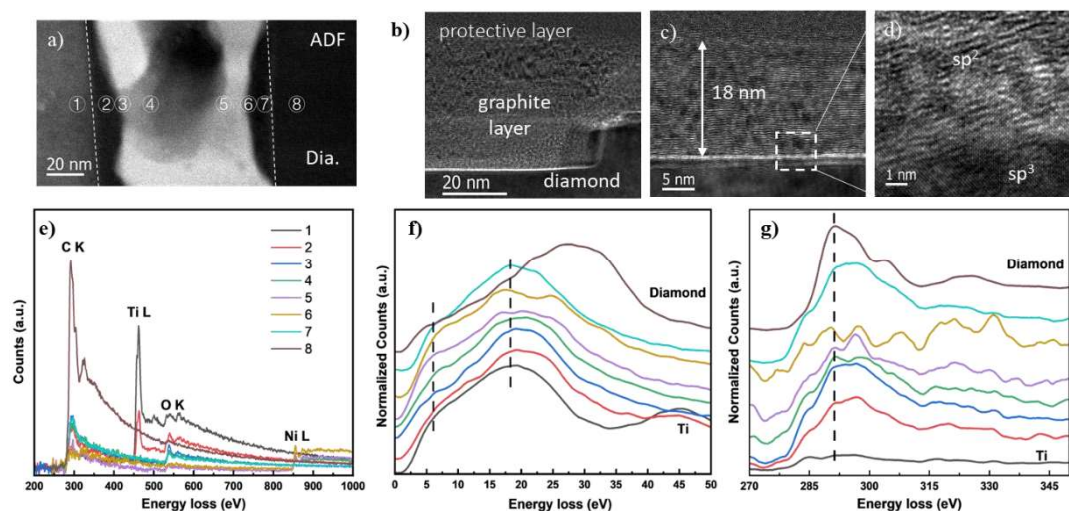


Figure 6

Captions:

Figure 1 Schematic diagram of GOD structure fabrication. (a) DC arc jet plasma equipment (b) Flow chart (c) Hall measurement using Van der Paw method.

Table 1 Hall measurements of GOD structure with different Ni thickness under 800 °C for 1.5 min.

Table 2 Hall measurements of GOD structure under different annealing temperature with 40 nm Ni film for 1.5 min.

Table 3 Hall measurements of GOD structure under different annealing time with 40 nm Ni film at 800 °C.

Table 4 Hall measurements of GOD structure under different diamond substrate with 40 nm Ni film at 800 °C for 1.5 min.

Figure 2 Raman spectrum of GOD structure. (a) p-type (b) n-type. I_G means the Intensity of G peak of graphene. $I_{\text{Dia.1st}}$ means the Intensity of first-order peak of diamond. Dia.2nd means the second-order peak of diamond.

Figure 3 XPS Spectrum of p-type GOD structure. (a) Survey (b) C1s (c) O1s (d) Ni2p

Figure 4 XPS Spectrum of n-type GOD structure. (a) Survey (b) C1s (c) O1s (d) Ni2p_{3/2}

Figure 5 TEM images and EELS spectrums of p-type GOD structure. (a) ADF image for line scan (b) HRTEM image (c) Zoom-in area (d) EELS line scan spectrum (e) Low loss of C K edge (f) High loss of C K edge

Figure 6 TEM images and EELS spectrums of n-type GOD structure. (a) ADF image for line scan (b) and (c) HRTEM images (d) Zoom-in area (e) EELS line scan spectrum (f) Low loss of C K edge (g) High loss of C K edge

CRedit author statement

Yuan Xiaolu: Data curation, Writing-Original draft preparation. **Liu Jinlong:** Methodology. **Liu Jiangwei:** Visualization, Investigation. **Wei Junjun:** Supervision. **Chen Liangxian:** Validation. **Wang Wenrui:** Resources, Writing-Review&Editing. **Li Chengming:** Conceptualization.

Acknowledgement

This work was supported by the National High-level University-sponsored Graduate Program of China Scholarship Council (CSC).

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Dear Editor and Reviewers,

We are truly grateful to yours kindly comments and thoughtful suggestions. Based on these comments and suggestions, we have made careful modifications on the original manuscript. All changes have made to the text are in red font with a yellow back. We hope the new manuscript will meet your comments and the magazine's standard. Below you will find our point-by-point responses to your comments/questions:

Reviewer #1: Dear Authors,

After correspondence, I recommend the manuscript for publication. I believe however that some of the answers would clarify the questions raised and further improve the manuscript if they partially were included in the text, e.g. (answer to Q4; "The results obtained in the tables are the average values of 3 samples taken under the same environment after 3 measurements for each sample").

Also some of the discussions regarding the n-type transport (Q9) could be included in the text.

Thank you very much for your kind reminder. Relevant sentences have been added in the manuscript and marked with red font. The modifications in manuscript are as follows:

In the "2. Methodology" section:

2.1 Preparation of GOD structure

The GOD structure was prepared by Ni-catalyzed diamond after fast annealing using direct current (DC) arc jet plasma equipment, as shown in Figure 1a. Compared to the normal rapid thermal annealing furnace, the DC arc jet plasma furnace has an extremely fast heating rate (>10 °C/s) and a relatively high vacuum (< 1 Pa). **The annealing process is completed instantaneously when the DC arc plasma is generated, contributing to the accurate control of annealing time,** which is helpful to obtain few-layer graphene, not multilayer graphite. **And the annealing temperature could be modulated by the arc power.** A detailed schematic diagram of GOD preparation process is displayed in Figure 1b. Firstly, several (100) orientation single crystal diamond substrates were polished and cleaned by mixed acid ($\text{H}_2\text{SO}_4:\text{HNO}_3=1:3$). The

1 surface roughness of Ra was below 1nm (20 $\mu\text{m}\times 20\text{ }\mu\text{m}$) for all diamond samples^[21].
2 Secondly, the metal catalysts were deposited on the surface of diamond substrates by
3 magnetron sputtering. The range of thickness for Ni films was set to 10 ~ 100 nm. Upon
4 incrementing the film's thickness, the catalytic Ni undergoes a phase transition from an
5 amorphous to a crystalline state, as demonstrated in Figure S1 (see Supplementary).
6 Then, the nickel-coated single crystal diamond samples were annealed under mixed
7 Ar₂/H₂ atmosphere. After rapid annealing, the nickel-coated single crystal diamond
8 samples were immersed in diluted acid (hydrochloric acid or nitric acid) until the
9 remaining Ni was completely dissolved.

10 **2.2 Characterization of GOD structure**

11 The Vander Paul method was used to measure the surface conductivity of the GOD
12 structure at room temperature using an Ecopia HMS-3000 instrument. Four gold
13 electrodes were deposited on the edge of GOD structure surface by photolithography
14 (Figure 1c). The applied magnetic field strength is 0.5 T. And the test current is set to
15 in the range of nA to mA. The results obtained in the tables are the average values of 3
16 samples taken under the same environment after 3 measurements for each sample. A
17 preliminary detection of the graphene structure on the diamond substrate was made by
18 Raman spectroscopy (Instrument: Renishaw inVia Qontor). The laser wavelength is 532
19 nm. The chemical states of C, O, Ni elements on GOD surface are characterized by X
20 ray photoelectron spectroscopy (XPS) (Instrument: ESCALAB Xi⁺). TEM (Instrument:
21 JEM-ARM300F) is used to observe the number of graphene layers and the interface
22 between graphene and diamond. Electron energy loss spectroscopy (EELS) is applied
23 to analyze the hybrid state of carbon atoms between diamond and graphene.

24 **In the “3. Methodology” section of last paragraph:**

25 For n-type GOD structure (Figure 6), multilayer graphene (or graphite) emerges
26 on diamond surface. The thickness of graphene is measured to approximately 18 nm. A
27 lot of Ni atoms embedded in diamond substrate, which is agreement to XPS
28 observations. In the low energy loss region, the plasma peak of diamond still shifts into
29 low loss region. While in the high energy loss region, a more complex bonding state
30 exists in Figure 6g, probably owing to the nickel-carbide inside the diamond.

1 Considering that the transport carriers of metal and graphite are both electrons, the
2 surface conductivity of GOD structure measured by Hall is a mixed structure of nickel-
3 carbide and graphite. Therefore, the main reason for n-type GOD structure is directly
4 attributed to nickel doping in the multilayer graphene (graphite). In contrast, p-type
5 GOD structures have few-layered graphene with clear interfaces and do not contain
6 nickel doping, which has been proved by XPS, TEM and EELS. Nevertheless, the
7 fundamental mechanisms of carrier transport on GOD structure are still unclear and
8 need to be further studied. A band diagram of two kinds of GOD structure might be
9 established to explain it.

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21 **Reviewer #2: No further comments.**

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23 Thank you very much for your support to this work.

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27 Once again, thank you very much for your kind and careful review. It is
28 appreciated greatly if you can consider our presentation for publication in *Diamond and*
29 *Related Materials*.

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35 Sincerely Yours,

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