

Graphene layers dependent vibrational property of metal-graphene heterostructures

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1. Introduction

Graphene proved interesting for nano-electronics and spintronics. There have been plenty of attempts to fabricate graphene devices. One of the key issues is controlling the charge injection / ejection phenomena at the interface between graphene and a metal electrode, for which the electronic structures at the metal/graphene interface should be elucidated. In the present study, interface-related phenomena and electronic structure of graphene in the metal/graphene heterostructures are investigated for the samples fabricated by metal deposition (Co, Ni, Ag and Au) and with various graphene layers numbers by employing confocal micro-Raman spectroscopy. In the graphene sheet made by microcleaving method [1], it has been reported that an unintentional hole doping to graphene occurs inhomogeneously even within the same graphene sample from the large variations of the Raman parameters by the position of the laser spot [2]. It is, therefore, necessary to exclude the influences of the inhomogeneous unintentional doping to the Raman spectrum for discussing the changes in the Raman parameters induced by metal deposition properly. For this purpose, we fabricated the specially arranged specimen with two region (the metal/graphene heterostructure region and the pristine graphene region), which are separated only by less than several μm on the same graphene sheet by using the micrometer patterned metal deposition with a shadow mask.

2. Experimental

Graphene sheet was transferred onto a glass substrate by microcleaving highly oriented pyrolytic graphite (HOPG). The prepared substrate (graphene/glass) was introduced into an UHV chamber with a base pressure of 3×10^{-7} Pa and was annealed at 423 K for 1h for degassing, and then the metal/graphene heterostructure was fabricated on a part of the graphene sheet by depositing a thin film (3-10 nm thick) of metals (Co, Ni, Ag and Au) and SiO_2 through a micro patterned shadow mask. The metals and SiO_2 were evaporated from electron beam evaporator (Co, Ni, Ag and SiO_2) and alumina coated tungsten basket (Au), respectively. The temperature of the glass substrate was kept at ambient temperature during the metal deposition. The surface of the metal film grown on the graphene sheet was capped

with 10 nm thick SiO_2 layer successively after the metal deposition, which assured the Raman analysis free from the influence of oxidation. A schematic representation and an optical micrograph of the metal/graphene sample are shown in Figure 1. The cross-section of the sample shown in Fig. 1 (b) has the structure of 10 nm- SiO_2 /5 nm-Co/graphene/glass in the heterostructure regions. The size of the heterostructure regions and the separated distance by the pristine graphene region are $7.5 \times 7.5 \mu\text{m}^2$ and $5 \mu\text{m}$, respectively.

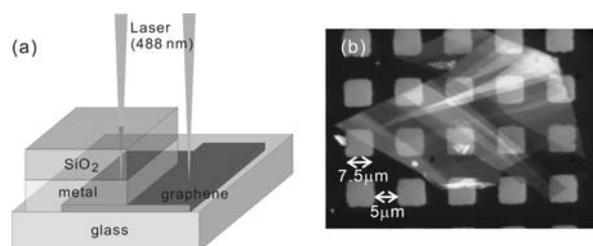


Fig. 1 (a) Schematic representation of specimen and (b) an optical micrograph of the Co/graphene sample with the structure of SiO_2 /Co/graphene/glass in the heterostructure region as an example. The graphene sheet contains several areas with different layers numbers.

The Raman measurements were carried out with a micro-Raman system (NANO-FINDER, Tokyo instruments) in a confocal backscattering geometry. Raman spectra were obtained by focusing Ar-ion laser (488 nm, 1 mW) to the selected spots with less than $1 \mu\text{m}$ diameter on the sample surface under ambient condition. The spectral resolution of the spectrometer was about 3 cm^{-1} . For the measurements of the heterostructure regions, Raman spectra were obtained through the metal film layer as depicted in Fig. 1 (a). The film thickness is thin enough for the probing laser penetration and detection of Raman signals through the metal layer. The micro-scale patterned structure of the metal/graphene specimen allows us to investigate the graphene layers number (n) dependences of the Raman parameters, since the graphene sheet contains several regions with different layers numbers as seen as the laminar contrast variation in the image of the graphene sheet in Fig. 1 (b). Changes in the Raman parameters; peak positions and the full width at the half maximum (FWHM) of the D, G and

2D bands, due to the formation of the metal/graphene heterostructure are examined by comparing a pair of the Raman spectra obtained at the neighboring two spots in the heterostructure and pristine graphene regions which are separated by only less than several μm .

3. Results and discussion

Figure 2 shows the systematic changes of the Raman peak position shifts of the G and 2D bands in the heterostructures region ($Pos_{\text{hetero}}(\text{G})$ and $Pos_{\text{hetero}}(\text{2D})$) from the positions in the adjacent pristine graphene region ($Pos_{\text{pri}}(\text{G})$ and $Pos_{\text{pri}}(\text{2D})$) of the Co/graphene and Au/graphene samples as a function of the number of graphene layers. The peak shifts of the G and 2D bands are denoted by " $Pos_{\text{hetero}}(\text{G}) - Pos_{\text{pri}}(\text{G})$ " and " $Pos_{\text{hetero}}(\text{2D}) - Pos_{\text{pri}}(\text{2D})$ ", respectively.

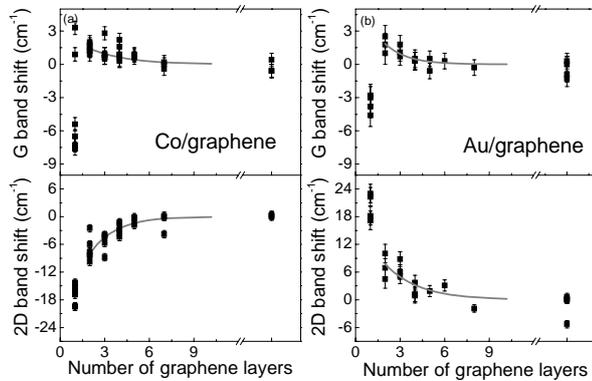


Fig. 2 Graphene layers number dependences of the Raman G and 2D band shifts by metal depositions; $Pos_{\text{metal}}(\text{G}) - Pos_{\text{pri}}(\text{G})$ (upper) and $Pos_{\text{metal}}(\text{2D}) - Pos_{\text{pri}}(\text{2D})$ (lower), evaluated for (a) the Co/graphene samples and (b) the Au/graphene samples.

In the heterostructures of the metal/multilayer graphene (MLG), the G band is stiffened (up-shifted) both in the Co/graphene and Au/graphene samples compared to the pristine graphene. Meanwhile, the 2D band is softened (down-shifted) in Co/graphene, whereas it is stiffened in Au/graphene. It has been reported that the doping of electrons / holes in a field effect geometry causes peak shifts of the G and 2D bands in graphene [3,4], and has demonstrated that the G peak is stiffened for both electron and hole doping, whereas the 2D peak is softened or stiffened for the respective doping types. Taking account of these correlations, the observed peak shift of the G and 2D bands in the MLG region are attributed to hole doping in the Au/graphene heterostructure and electron doping in the Co/graphene heterostructure, respectively. It is worthy to note that the type of doped carriers cannot simply predict from the work functions of metals and graphene, since the quantities are almost the same in between Co (5.1 eV) and Au (5.0 eV) [5], and hence one can expect that holes tend to be doped in both heterostructures taking account of the work function of graphene (4.6 eV) [6]. The present results indicate that the type of carrier doping in the met-

al/graphene heterostructures is affected by the chemical /electronic interactions at the metal/graphene interface.

In Fig.2, it is also found that a remarkable difference in the G band shifts arises between the metal/graphene heterostructures made of single layer graphene (SLG) and MLG. In order to explain the different directions of the G band shifts (up- / down-shifts) in between the metal/SLG and metal/MLG heterostructures as shown in Fig. 2, it is necessary to assume different contributions to the shifts of the Raman parameters depending on single layer or multilayer ($n \geq 2$), or the negligibly small signals from the first graphene layer at the interface compared with the signals from the other layers. The latter possibility, however, can be excluded at least for the Au/graphene heterostructures in which Au exists as grains with 20-100 nm diameters, because, under such situation, surface enhancement effect of Raman scattering is expected to occur within the distance of several nm ($n \sim 10$) from the interface [7]. Furthermore, considering that the quantities of the G band shifts in the heterostructures are well fitted with simple exponential decay as a function of the number of graphene layers within the range of $n \geq 2$ both for the Co/graphene and Au/graphene heterostructures, it is surmised that the interfacial interaction between metal and graphene changes from the strong chemical interactions whose fashion is suggested to depend on metal species in the metal/SLG heterostructures to the weaker ones in the metal/MLG ($n \geq 2$) heterostructures in which the changes of the Raman parameters are predominantly affected by carrier doping.

4. Conclusions

Raman parameter changes in the heterostructures depending on metal species and graphene layers number revealed the followings: (i) Characteristics of charge carrier doping into the graphene layer; carrier doping within the critical thickness of a few graphene layers from the interface and the dope type change (electron / hole doping) reflecting not the vacuum level shift but the interfacial interaction. (ii) Different interfacial interactions in between single layer and multilayer graphenes; strong chemical interactions at the metal/SLG interfaces even in the case of Au and their decay in multilayer graphene.

References

- [1] K.S. Novoselov et al., Proc.Natl.Acad.Sci. **102** (2005) 10451.
- [2] C. Casiraghi et al., Appl. Phys. Lett. **91** (2007) 233108.
- [3] J. Yan et al., Phys. Rev. Lett. **98** (2007) 166802.
- [4] S. Pisana et al., Nat. Mater **6** (2007) 198.
- [5] H.B. Michaelson, J. Appl. Phys. **48** (1977) 4729.
- [6] C. Oshima and A. Nagashima, J. Phys. Condens. Mater **9** (1997) 1.
- [7] G.J. Kovacs et al., Langmuir **2** (1986) 689.