Raman study on few-layer graphene pressurized in hydrogen gas

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Keywords: few-layer graphene, hydrogen, high pressure, Raman spectroscopy

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Atomic-layered materials, graphene, having a honeycomb-lattice structure caused by sp^2 hybridized orbitals between carbon atoms, results in π-electron system with a band gap of zero [1]. Transferring of graphene onto a SiO_2/Si substrate leaded to the discoveries of various novel properties of graphene such as electrical conduction [2], optical properties [3] and anomalous quantum Hall effect [4,5].

Functionalization of graphene courses the change in electrical properties [6-8] because of its huge specific surface area. Graphene is however inactive, so we need to activate by some kinds of methods. Hydrogenation of graphene was demonstrated by radio-frequency hydrogen-plasma or heating in hydrogen (H_2) gas at 200 ºC under pressure of 2.6 to 5.0 GPa [9]. In addition, annealing of hydrogenated graphene at modest temperature removed H atoms [10,11]. It suggests that a weak bond between graphene and H atoms could be utilized for replacing H atoms with other functional groups. In addition, it was revealed that hydrogenation of graphene drastically reduces its electrical conductivity.

To investigate the effect of pressure on electron states of few-layer graphene in an atmosphere wherein H_2 coexists, the stretching and rotational vibration bands of H_2 and G-band were observed *in situ*. We also searched the possibility of hydrogenation of few-layer graphene under high pressure at room temperature; utilizing H_2 intercalated into interlayer space was examined as the source of hydrogenation. This is based on a recent study on the intercalation of hydrogen into interlayer space of graphite at pressures above 10 GPa and room temperature [12].

Diamond anvils of type Ia with 0.6 mm and a thickness of 2.0 mm, were used for not only generation of pressure but also a supporting substrate of graphene. The first-order Raman scattering intensities of diamond decrease with an increasing number of layers due to 2.3% opacity of visible light per layer [3]. We are able to count the number of layers of graphene based on a ratio of peak heights, $I_n/I_0 = 0.977^{2n}$, where I_n and I_0 are the peak heights from the diamond anvil substrate masked by n-layer graphene and the bear one before masking, respectively [13]. The gaskets were made of less than 70-μm-thick rhenium and/or tungsten, in which 300-μm holes were drilled. Some pieces of few- layer graphene were exfoliated from Kish graphite with masking tape and transferred to the upper side of diamond anvil. We could obtain 3- to 14-layer graphene on the culet surface. Ruby balls as the pressure markers were put in the gasket holes mounted on the culets of lower anvils, which were filled with high-density H_2 gas. Each pressure was determined from a fluorescence peak of the ruby balls on the basis of ruby pressure scale [14].

Few-layer graphene was pressurized in the state of coexisting with H_2 up to 21 GPa at room temperature, and Raman spectra were measured at each pressure. A 180º back scattering geometry was employed for the observation. An excitation wavelength of 514.5 nm was provided by an Ar^+ ion laser. The spectra were obtained using a microscopic Raman spectrometer, which had a single monochromator with a 4 cm^{-1} resolution (Jobin Yvon/ ATAGO BUSSAN CO. LTD., T6400), and a liquid nitrogen cooled charge-coupled device (CCD) detector. The laser beam was focused to a 1.25 μm spot on the sample, at which the laser power was roughly less than 10 mW for the samples with the diamond anvil substitute.

Pressure change in G-band of 7-layer graphene is shown in Figure 1. A loading process shown in (a) causes

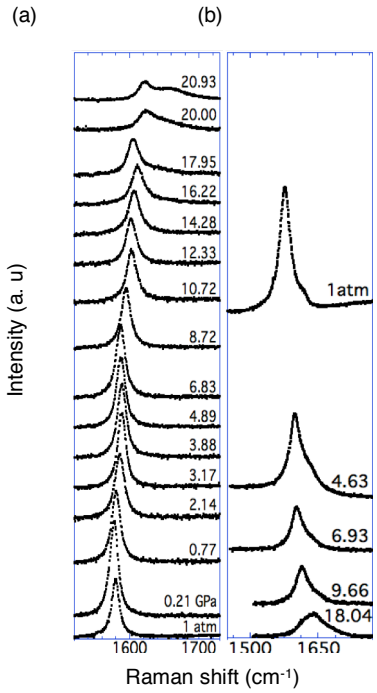

Figure 1. Pressure change in G-band of 7-layer graphene. (a) and (b) were obtained in the loading and unloading processes, respectively.

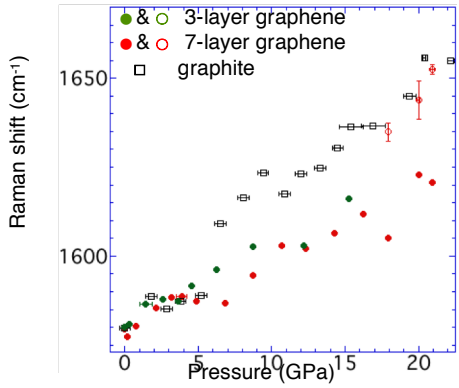

Figure 2. Pressure changes in Raman shift of G-band for 3- and 7-layer graphene and graphite loaded in H_2 gas, obtained in the loading process.

the increase of linewidth under pressure higher than 7 GPa.

Anomaly of the pressure change in the Raman shift and anti-symmetrization of the line shape were observed at 17.95 GPa; the peak-splitting was clearly generated at 20.93 GPa. The symmetrical line shape of G-band could not revive by unloading the pressure; the released sample gave the D' band at around 1620 cm^{-1} generated by the presence of defects, in addition to G-band corresponding to E_{2g} mode. We could not catch D-band because the diamond anvil is used for the substrate of graphene which is transparent.

The pressure changes in G-band of 7-layer graphene showed parabolic change with the maximum of Raman shift at around 4 GPa under pressure lower than 7 GPa. Such a behavior was also observed in the rotational band of H_2 obtained at the focal spot on the graphene. It suggests that the solidification of H_2 [15] is reflected in the lattice vibration of graphene. In addition, the pressure dependence occurs anomalies at around 11 GPa and 18GPa. According to the confocal micro-Raman spectroscopy of graphite, it is reported that pressure-induced intercalation of H_2 occurs at around 10 GPa at room temperature [12]. Our usual micro-Raman study, unfortunately, could not catch the extra bands based on H_2 stretching vibration. On the other hand, not only 7-layer graphene but also 3-layer graphene and graphite showed anomaly of the change at around 10 GPa. Therefore it is considerable that the intercalation is also caused in few layer graphene, and that we are ready to cause the hydrogenation of graphene using the intercalant H_2. The anomaly observed at around 17.95 GPa were obtained in the all samples ranging from 7- to 14-layer graphene. The clear band splitting was observed in only 7- and 13-layer graphene. We cannot find the regularity of the number of layers at present.

Graphite is known to cause pressure-induced phase-transition at around 18 GPa [16,17]. According to the first-principle calculation, the transition is expected to be originated from buckling of graphene [18]. It is considered that the anomaly observed at around 18 GPa is derived from the buckling phenomenon. If the phase transition causes at the pressure around 18 GPa, Raman intensity and line with of G-band drastically decreases, resulting in the transition to hexagonal diamond [16,17]. Our result however didn't show such behaviors in both graphite and few-layer graphene. When H_2 is intercalated in the interlayer space, it is expected that high density state of H_2 is generated there. It seems that enhancing of the intermolecular repulsion between H_2 molecules and interatomic one between C atoms interrupts the buckling of graphene. Even if graphene causes the buckling, it is difficult to make sp^3 bond between C atoms due to loss of nearest neighbor graphene layers by interrupting of H_2. In short, the presence of H_2 in the interlayer space may play a role of disturbing the phase transition. Therefore H_2 molecules closing to C atoms on graphene, attach to graphene from the two opposite side, and C atoms deviate from the plane, resulting in buckling. Under pressure above 18GPa, diversified few-layer graphene showed the anti-symmetrized line shape of G-band, moreover, the released sample maintained he anti-symmetrized one. We propose that is one of the evidences of hydrogenation of few-layer graphene.

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