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Electronic Properties and Impurity-Induced States of Hexagonal Boron Nitride Layers: A First-Principles Study

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Two-dimensional (2D) atomic-layered materials, including graphene and hexagonal boron nitride (h-BN), have been actively studied from both theoretical and experimental perspectives since they have unique and outstanding properties. Furthermore, new physical properties can be obtained by constructing van der Waals heterostructures which are artificially stacked materials consisting of different 2D atomic-layered materials. Graphene is a significant material not only in physics but also in applications to electronic devices. h-BN also has a honeycomb lattice structure consisting of boron and nitrogen atoms similar to graphene. However, graphene shows metallic behavior, while h-BN is a semiconductor material with a wide band gap. It is known that the h-BN is an excellent substrate for graphene and other 2D atomic-layered materials. h-BN attracts much attention not only as a substrate material but also itself as future nanoelectronics material. In semiconductors, defects play an essential role since they often determine the electronic properties of the system. Therefore, it is of high importance to theoretically investigate how an impurity doped in h-BN affects the electronic properties of the graphene/h-BN heterostructures as well as h-BN thin layers. In this thesis, we study the geometric and electronic properties of graphene/h-BN heterostructures and h-BN thin layers, including h-BN monolayer, and their doped system, using first-principles calculations within the framework of the density functional theory to clarify the electronic structure and impurity-induced states in the h-BN layers. The results presented in this thesis could guide experiments for future device applications based on 2D atomic-layered materials.

The scanning tunneling microscopy (STM) is known to be a powerful method for observing the electronic states in the 2D atomic-layered materials and their doped system. We study electronic structures and STM images of the graphene/h-BN heterostructures and their C-doped system. In the heterostructure consisting of graphene and h-BN monolayer, we study four types of different stacking structures, including a rotated system as a model of a lattice-mismatched system. It is found that the impurity C atom doped in the h-BN layer at the B site and the N site gives asymmetric charge carrier densities in the graphene layer. It is also found that electronic states of the system up to the surface graphene layer are modulated by the carbon impurity at the N site in the underlying h-BN substrate. As a result, the doped carbon impurity at the N site can be visualized as a bright spot in the STM images, even in

the case of the doped C atom in the deep h-BN layer from the surface graphene layer. On the other hand, the carbon impurity at the B site in the h-BN layer essentially does not change the STM image over the surface graphene layer even if the C atom is doped in the h-BN layer next to the surface graphene layer. We show that the difference between the effects caused by the doped carbon impurities at the B site and the N site on the STM images is due to the spatial distributions of the local density of state induced by the doped carbon atom.

We also study the stabilities and electronic properties of the thin h-BN layers. We clarify the relative stabilities of the thin h-BN layers with various stacking sequences. We show the rich variations of the electronic structure (band gaps and its transition type etc.) depending on the stacking sequences of the thin h-BN layers. Furthermore, we study the effects of the doping of a carbon atom on the electronic states of the thin h-BN layers. It is found that a relatively shallow impurity state can be induced by a doped carbon atom in the h-BN trilayer with a specific stacking sequence. Moreover, it is also found that spatial distributions of the electronic states in the conduction band minimum and the valence band maximum are localized in certain h-BN layers. Using this result, we can separate the carrier conducting layers from the doped h-BN layer in several stacking sequences. This separation indicates the possibility of modulation doping in the thin h-BN layers. We also show that modulation doping becomes possible for both donors and acceptors in the three or more h-BN layers.

Finally, we study the electronic properties of the doped h-BN monolayer using first-principles calculations based on the hybrid functional approach. One of the crucial problems in the density functional theory is that the local density approximation (LDA) and the generalized gradient approximation (GGA) underestimate the band gap and ionization energy of an impurity-induced state in semiconductors. Hence, it is difficult to predict them accurately. It is known that hybrid functionals improve over the LDA and the GGA in the prediction of these values in the three-dimensional semiconductors. In this study, we apply Heyd-Scuseria-Ernzerhof (HSE) hybrid functional to the doped h-BN monolayer. Furthermore, the mixing parameter between local (semi-local) and non-local exchange in the HSE hybrid functional and screening parameter are optimized to satisfy the generalized Koopmans' theorem (gKT). Using this approach, we study the ionization energies of impurity states induced by a carbon atom or an oxygen atom in the h-BN monolayer. It is found that the ionization energy of the doped oxygen atom at the N site is smaller than those of the carbon atom at the B site and N site.