§30. Theoretical Study on Hydrogen Negative Ion Formation on Metal Surfaces

Kasai, H. (Osaka Univ.)

High yield production of negative hydrogen ions is demanded for the use in nuclear fusion applications. The negative ions are used as ionizing reactants in proton beam accelerators and heating sources in nuclear fusion reactors. Work function has been considered as a key factor that qualitatively determines the efficiency of the negative ion production in the surface production method[1]. However, highly oriented pyrolytic graphite (HOPG) was reported as the exceptional case; nevertheless of its relatively high work function (ca. 5 eV), the yield of negative ion production is comparable to the case of a low work function material (ca. 2 eV), Cs/W(110) surface[2].

In order to completely describe the process for the negative ion production, more explicit theoretical treatments are then required. As a factor affecting the rate of the negative ion production other than work function, level broadening of electronic states of hydrogen near the surface would contribute to the ionization. Electron transfer from the conduction band of the surface to the electron affinity level can proceed when the affinity level is appeared in the Fermi level by the broadening. Time-dependent hydrogen-surface interactions with dynamical consideration of the electron excitations are necessary for describing the ionization.

As the simple but purely theoretical method which does not require experiments for determining the parameters, we developed a combined method; ab initio calculations based on density functional theory and Newns-Anderson model[3]. In the ab initio calculations, the project augmented plane wave (PAW) method[4] with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[5] are used within Quantum Espresso package code[6]. The Kohn-Sham orbitals are expanded in a plane wave basis with energy cut-off of 680 eV. Brillouin zone integrations are performed with 8×8×1 sampling meshes. As the model for the ionization on HOPG, a perpendicularly approaching hydrogen atom to a graphene sheet is considered. The unit cell used contains 8 carbon atoms and 1 hydrogen atom. Each sheet is separated by a vacuum layer of 15.875 Å thickness. Newns-Anderson model considers the effective Hamiltonian[7] of hydrogen-surface system given by

$$H = \sum_{k,\sigma} \varepsilon(k) a^{\dagger}_{k,\sigma} a_{k,\sigma} + \sum_{a,\sigma} \varepsilon_a a^{\dagger}_{a,\sigma} a_{a,\sigma}$$
$$+ \sum_{k,a,\sigma} [V_{k,a} a^{\dagger}_{k,\sigma} a_{a,\sigma} + h.c.] + \frac{U}{2} \sum_{a,\sigma} \varepsilon_a a^{\dagger}_{a,\sigma} a_{a,\sigma} a^{\dagger}_{a,-\sigma} a_{a-,\sigma}$$

where ε(k) is the energy dispersion of the surface, ε_a is the energy levels of hydrogen atom, $V_{k,a}$ is the hybridization strength between hydrogen and surface state, and U is the intra-atomic Coulomb interaction. The hybridization term explicitly incorporates time as the variable. The time dependence is classically introduced by considering the trajectory. Equations of motion for the three species, negative ion, neutral atom, and positive ion, are solved self-consistently[8]. The value of $V_{k,a}$ is estimated by referring the level broadening in the density of states (DOS) obtained in ab initio calculations.

The level broadening behavior is shown in Fig. 1. The atomic levels (indicated red peak in Fig. 1) are found to be broadened so that electron occupation in the affinity is partly observed.

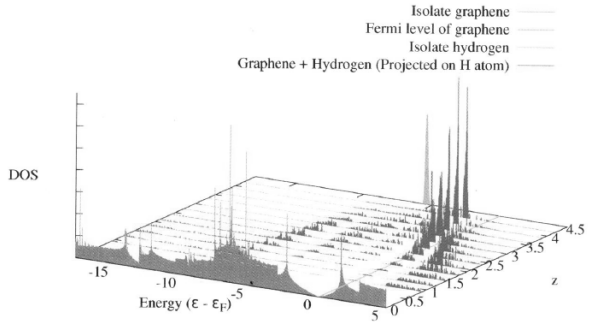

Fig.1. Density of states and projected density of states along the height of hydrogen perpendicularly approaching to top-site.

The time-evolution of the charged species obtained by solving Newns-Anderson model is shown in Fig. 2. Negative ions (indicated by light blue curve in Fig. 2) are found to be produced in our simulation.

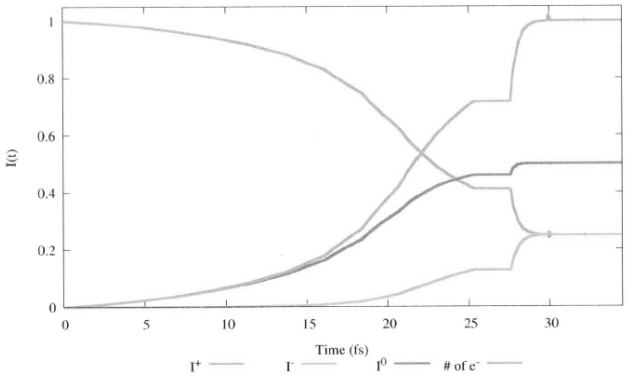

Fig.2. Time-evolution of charged state (negative ion I^-, neutral atom I^0_σ, positive ion I^+) along the height of hydrogen perpendicularly approaching to top-site.

Towards rational designs of the material for negative ion production, our method allows us to analyze the aspects of both static and dynamic quantum behaviors of the material. We believe that this progress is the first step for the comparative theoretical prediction in future.

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