

Tight-Binding Theoretical Study of Monolayer h-BN on Ni (111) Surface

S SAHU¹ and G C ROUT^{2,*}

¹School of Basic Sciences (Physics), IIT Bhubaneswar, Odisha, India

²Condensed Matter Physics Group , Physics Enclave, Plot No.- 664/4825,Shree Vihar, C.S. Pur , PO-Patia , Bhubaneswar- 751031, Odisha, India
Corresponding email: *profgcrou@gmail.com

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Abstract. We present here a tight-binding calculation of the band structure of monolayer hexagonal boron nitride (h-BN) on NI (111) substrate taking into account of electron hoppings upto third nearest neighbour. Here h-BN is placed over a single layer of ferromagnetic ordered Ni in which the nitrogen atom of the honeycomb lattice of h-BN layer lies on the Ni atom of the bottom layer. Due to close matching of the lattice constants between h-BN and Ni, the hybridization between $2p_z$ orbital of N and $3d_{z^2}$ orbital of Ni is expected to be relative stronger. Further the ferromagnetism in Ni arising due to spin dependent electrostatic exchange interaction is also taken into account. All these above effects are incorporated in the tight-binding Hamiltonian. The magnetization in Ni layer is computed self-consistently. Finally the band structure of the system is calculated and the results are discussed to interpret the experimental data.

Keywords: h-BN-Nickel (111) system, Green's function, Magnetization, Tight-binding method

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1. Introduction

Thin insulator ultra-thin films weakly bonded to flat metal surfaces would be attractive in the field of fabrication of microelectronic devices such as tunneling devices because of the spatially abrupt change of the electronic structure at the interface. Hexagonal boron nitride (h-BN) is an insulating material which is iso-structural to semi-metallic graphite. Much attention has been paid to h-BN in relation to its technological applications[1]. In h-BN, the boron and nitrogen

atoms construct a two-dimensional (2D) honeycomb structure with strong covalent bonds, while the basal planes interact weakly with each other via Van der Waals bonds (with slightly ionic bonds). Therefore, h- BN exhibits strongly anisotropic character in many physical properties such as energy band structure, electrical conductivity, thermal conductivity, Debye temperature etc. [2]. Uniform monolayer films of hexagonal-boron nitride (h-BN) is grown in a commensurate manner on the Ni (111) surface with a 1×1 atomic structure [2]. There, the in-plane lattice constant of h-BN shrinks by 1.4 % to match the Ni-Ni spacing of the topmost Ni layer. On Ni (111), it forms an atomically sharp, almost perfect over-layer. The h-BN/Ni(111) is thus a prototype system for the study of magnetic metal insulator interfaces.

The structural model for the monolayer h-BN on Ni(111) has been proposed as a result of low-energy electron diffraction(LEED) intensity analysis[3]. It has been suggested that the h-BN layer is rumpled (B atoms slightly below N atoms), with N atoms atop the outermost Ni atoms. This model has been confirmed in the x-ray photoelectron diffraction and scanning tunneling microscopy (STM) study by Auwärter et al.[4] and in the recent density-functional theory (DFT) investigation by Grad et al.[1].

In the present Communication, we report here the magnetization in nickel monolayer and its effect on induced magnetization in h-BN by tight-binding mean- field approach. We present the formalism of the h-BN/nickel (111) system in section 2, the calculation of the Green's function and the induced magnetization in section 3, results and discussion in section 4 and finally conclusion in section 5.

2. Tight-binding model Hamiltonian

Earlier we proposed a tight-binding model Hamiltonian for graphene-on-monolayer nickel atoms [5]. Similar tight-binding Hamiltonian is employed here for insulating h-BN monolayer on monolayer Ni atoms. Here the two sub-lattice Carbon atoms are replaced by boron and nitrogen atoms. The h-BN/nickel (111) system consists of single layer of h-BN over one layer of nickel (111). The single particle Hamiltonian for upper layer h-BN is given by

$$H_1 = \sum_{k,\sigma} [\varepsilon_N(k) a_{k,\sigma}^\dagger a_{k,\sigma} + \varepsilon_B(k) b_{k,\sigma}^\dagger b_{k,\sigma}] + \sum_{\alpha,k} [\varepsilon_{13}(k) a_{k,\sigma}^\dagger b_{k,\sigma} + \varepsilon_{13}^*(k) b_{k,\sigma}^\dagger a_{k,\sigma}] \quad (1)$$

Here the first part of Hamiltonian H_1 contains energies $\varepsilon_N(k) = \varepsilon_N + \varepsilon_{2k}$ and $\varepsilon_B(k) = \varepsilon_B + \varepsilon_{2k}$ for nitrogen and boron atoms in h-BN. Here $\varepsilon_N/\varepsilon_B$ and ε_{2k} are the site energies of N/B and the second nearest-neighbor hopping energies of electrons between N and B atoms. The electron operators $a_{k,\sigma}^\dagger(a_{k,\sigma})$ and $b_{k,\sigma}^\dagger(b_{k,\sigma})$ are the creation (annihilation) operators at two lattices of h-BN. The second part of Hamiltonian H_1 consists of hopping of electrons between inter site sub-lattices having dispersion energy $\varepsilon_{13}(k) = \varepsilon_{1k} + \varepsilon_{3k}$; here ε_{1k} and ε_{3k} are respective electron dispersion energy of nearest- neighbor and next-to-next nearest-neighbor electron. The Hamiltonian for monolayer nickel (111) can be written as

$$H_{Ni} = \sum_{k,\sigma} \left[E(k) + \frac{U}{4} \sigma m \right] c_{k,\sigma}^\dagger c_{k,\sigma} \quad (2)$$

Here H_{Ni} represents the Hamiltonian for nickel (111) having band dispersion energy $E(k)$. U , m and σ are the onsite Coulomb potential, intrinsic magnetization for both the spins within mean-field approximation of the Coulomb correlation interaction between electrons. Here $c_{k,\sigma}^\dagger(c_{k,\sigma})$ is the creation (annihilation) electron operator at the nickel site. When h-BN is placed over nickel (111), there may be charge transfer and the p-d hybridization between the 3d electron of Ni and p electron of nitrogen at h-BN-metal interfaces. Then the interlayer Hamiltonian for h-BN-metal system is given by

$$H_\perp = \sum_{k,\sigma} [\varepsilon_{pN}(k) a_{k,\sigma}^\dagger c_{k,\sigma} + \varepsilon_{pN}^*(k) c_{k,\sigma}^\dagger a_{k,\sigma}] \sum_{k,\sigma} [\varepsilon_{pB}(k) b_{k,\sigma}^\dagger c_{k,\sigma} + \varepsilon_{pB}^*(k) c_{k,\sigma}^\dagger b_{k,\sigma}] \quad (3)$$

The Hamiltonian H_\perp represents the hopping of electrons from first layer to second layer and vice-versa with interlayer hopping energy $\varepsilon_{pN(B)}(k)$. The total Hamiltonian is given by $H = H_1 + H_{Ni} + H_\perp$.

3. Calculation of Green's functions and magnetization in h-BN/nickel system

In order to calculate the physical parameters, we calculate the three coupled electron Green's functions involving electrons of h-BN at nitrogen site. They are defined as $A_1(k, \omega) = \ll a_{k,\sigma}; a_{k,\sigma}^\dagger \gg_\omega$, $A_2(k, \omega) = \ll b_{k,\sigma}; a_{k,\sigma}^\dagger \gg_\omega$ and $A_3(k, \omega) = \ll c_{k,\sigma}; a_{k,\sigma}^\dagger \gg_\omega$. Similarly we can define the Green's functions involving electrons at boron site of h-BN and Ni (111) which are not shown explicitly. The coupled Green's functions are solved by Zubarev's technique[6]

and we found $A_1(k, \omega) = \frac{a_{11}}{2\pi|D(\omega)|}$ and $B_1(k, \omega) = \frac{b_{11}}{2\pi|D(\omega)|}$ for h-BN and $C_1(k, \omega) = \frac{c_{11}}{2\pi|D(\omega)|}$ for nickel. Here a_{11} , b_{11} and c_{11} are not given explicitly and $|D(\omega)|$ is written as $|D(\omega)| = a\omega^3 + b\omega^2 + c\omega + d$. As the equation is a cubic in ω , which is solved numerically by equating the denominator term to zero i.e. $|D(\omega)| = 0$. We can obtain three quasi-particle band dispersion energies $\omega_{\alpha,k,\sigma}$ for $\alpha = 1, 2, 3$ by taking 1000×1000 grid points of the electron momentum in XY plane. Here $a = 1$, $b = -[\varepsilon_N(k) + \varepsilon_B(k) + (E(k) + \frac{U}{4}\sigma m)]$, $c = (\varepsilon_N(k) + \varepsilon_N(k)) \left(E(k) + \frac{U}{4}\sigma m \right) + \varepsilon_N(k)\varepsilon_B(k) - |\varepsilon_{pN}(k)|^2 - |\varepsilon_{13}(k)|^2$, $d = \varepsilon_B(k)|\varepsilon_{pN}(k)|^2 + \left(E(k) + \frac{U}{4}\sigma m \right) |\varepsilon_{13}(k)|^2 - \varepsilon_N(k)\varepsilon_B(k) \left(E(k) + \frac{U}{4}\sigma m \right)$. We have obtained three electron bands w_{1k} , w_{2k} and w_{3k} for h-BN-nickel hybrid system. The intrinsic magnetization in nickel is given as $m = -(n_{\uparrow}^{Ni} - n_{\downarrow}^{Ni})$, where $n_{\sigma}^{Ni} = \sum_{\alpha=1-3} f(\beta\omega_{\alpha,k,\sigma})k_{\alpha}(\omega_{\alpha,k,\sigma})p_{\alpha}$. The expression of p_{α} is not shown explicitly [5].

4. Results and Discussion

There appears a difference between the electron occupancies between the up and down spin electrons at Ni site leading to ferromagnetic magnetization (m) in the Ni layer. The magnetization (m) calculated in section 3 is computed numerically and self consistently. Finally these band dispersion energy, $w_{\alpha,k}$ with $\alpha = 1, 2, 3$ for upspin are plotted in figure1 for graphene on monolayer Ni and monolayer h-BN on monolayer Ni. For graphene/Ni (111) system, we observe three bands w_{1k} , w_{2k} and w_{3k} shown by dotted lines in figure1. The two bands w_{1k} and w_{2k} touch each other at Γ point indicating that there is no direct interaction between $2p$ carbon orbital at B sub-lattice site (represented by w_{1k}) and Ni $3d$ orbitals (represented by w_{3k}). Since pd interaction is considered in the Hamiltonian in equation (3), there occurs a weak hybridization between $2p$ orbitals of carbon at A sub-lattice (represented by w_{3k}) and $3d$ Ni orbitals. Hence there appears a gap of magnitude 0.13 eV at K point and M point [5].

For h-BN/Ni (111) system of the present interest, we plot the three band dispersions w_{1k} , w_{2k} and w_{3k} for up spin in figure 1 as shown by continuous lines. Since the nitrogen atom is placed just above the Ni atom, there occurs a strong hybridization between the electrons of nitrogen and Ni atoms. Hence a large band gap is expected between this bands w_{2k} (representing by Ni orbitals) and w_{3k} (representing by Ni orbitals). As shown in figure1, we observe

comparatively large band gap of about **2.745 eV** between this two bands at K point (Fermi) and M point of the system (see figure 1). Such types of band gap are reported earlier in the dynamic mean-field (DFT) calculation under the local density approximation (LDA) for the system monolayer h-BN on Ni (111) [7]. Further it is observed that the minima of the π -band w_{2k} lies at energy ~ -9.5 eV at Γ point and its maxima lies at ~ -4.0 eV resulting in the formation of band width of ~ 5.0 eV. The experimental photoemission dispersion plot of h-BN/Ni shows that the π -band width of ≈ 5.5 eV and the spin averaged theoretical width ≈ 5.52 eV [1]. Further our present calculation is in

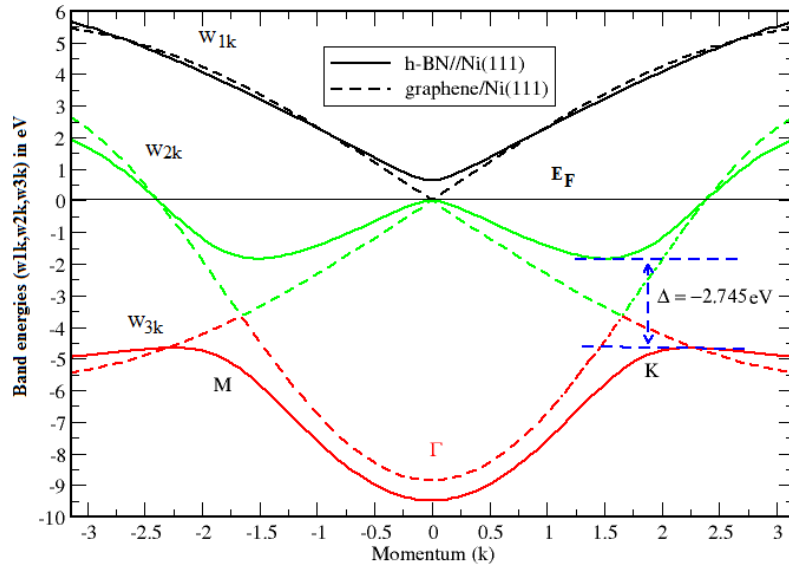


Fig. 1. Plot of band energies vs. momentum of h-BN//Ni(111)(continuous lines) and graphene/Ni(111) (dashed lines)

fair agreement with the photo emission experiment gap 5.8 eV for this system by Nagashima et al. [8,9]. It is to note further that the upper π -band w_{1k} and Ni band w_{2k} exhibit a band gap of order ≈ 1 eV at Γ point in contrast to zero band gap at Γ point reported for graphene-on Ni system [5].

5. Conclusion

We report here a tight-binding model calculation for band structure of monolayer h-BN/Ni (111) system by using Zubarev's Greens function technique. We observe that the Dirac point is shifted to the electron momentum $\frac{\pi}{2}$, where there appears a band gap of **2.745 eV** for h-BN/Ni system which is much

smaller than the band gap of **5.9 eV** for pristine h-BN system [10]. Further the h-BN/ Ni system behaves as large band gap semiconductor. Hence it is expected that there is some charge transfer between Ni layer and N atom of the h-BN layer.

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