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Platinum Adsorption and Diffusion on Two-Dimensional Gallium Nitride

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Abstract: In this study, we examined the adsorption and diffusion of platinum (Pt) adatom on two-dimensional hexagonal gallium nitride (h-GaN), by using first-principles plane-wave calculations. Two different levels of platinum coverage ratio (θ=1/8 and θ=1/32) were considered and the changes in the electronic structure for high-level platinum coverage ratio (θ=1/8) were examined. Low-level coverage ratio (θ=1/32) is used to calculate the diffusion barrier energy of Pt adatom on GaN monolayer. Our theoretical calculations have shown that Pt atom strongly binds on the top of nitrogen atoms in GaN monolayer and high energy is required for its diffusion. While GaN monolayer has 2.1 eV indirect band gap (Γ→K), this band gap reduces to 1.3 eV with Pt adsorption. These results may lead to further investigations on forming Pt nanoparticles or Pt coating on GaN sheet.

İki Boyutlu Galyum Nitrat Üzerinde Platin Adsorpsiyonu ve Difüzyonu

Anahtar Kelimeler
Yoğunluk fonksiyoneli teorisi,
Pt adsorpsiyonu,
Galyum nitrat,
İki boyutlu malzemeler

Özet: Bu çalışmada ilk prensipler düzlem dalga hesaplamaları temelinde platinyum atomunun iki boyutlu altıgen galyum nitrat (h-GaN) üzerindeki adsorpsiyonu ve difüzyonu incelendi. İki farklı platin kaplama oranı (θ = 1/8 ve θ = 1/32) dikkate alındı ve sadece yüksek seviyeli platin kaplama oranı (θ = 1/8) için elektronik yapıdaki değişiklikler incelendi. GaN tek tabakası üzerindeki Pt atomunun difüzyon bariyer enerjisini hesaplamak için düşük seviyeli kaplama oranı (θ = 1/32) kullanıldı. Teorik hesaplamalar, Pt atomunun GaN tek tabaka içindeki nitrojen atomlarının üstünden güçlü bir şekilde bağlandığını ve onu oradan difüze etmek için yüksek enerjiye ihtiyaç olduğunu göstermektedir. GaN tek tabakası, 2.1 eV doğrudan olmayan bant aralığına (Γ→K) sahip iken, bu bant aralığı Pt adsorpsiyonu ile 1.3 eV'ye düşmüştür. Bu sonuçların, gelecekte GaN tabakası üzerinde Pt nanopartiküllerin oluşturulması ya da Pt ile kaplanması üzerine çalışılmasının önünü açabileceği düşünülmektedir.

1. Introduction

Gallium nitride (GaN) can be found in cubic zincblende or wurtzite crystal structures. Both of them have a wide band gap in the range of 3.30 – 3.50 eV [1, 2]. Owing to their band gap, GaN structures are the most commonly used semiconductors in optoelectronic device applications, e.g., fabrication of light-emitting diodes (LED) to operate in blue-light and ultraviolet regions, room temperature laser diodes, high temperature/high power electrical devices [3, 4]. In addition to its wide band gap, GaN is a chemically and thermally stable semiconductor material, which preserves its structural stability up to temperatures above 1100K [5]. Meanwhile, researchers are also concentrated on designing future catalysts and gas sensors utilizing high efficiency of group III-nitrides [6]. GaN-based Schottky diodes [7] and field-effect transistors (FETs) [8] have been used as gas sensors. GaN hydrogen gas sensors have been fabricated which have displayed a wide-range hydrogen sensing capability [9]. Cobalt-doped hexagonal boron nitride (h-BN) monolayer was investigated by Lin et. al., who found low CO oxidation barriers with the Eley−Rideal mechanism, which may attribute the Co-doped BN a viable catalyst for CO oxidation [10]. As known from electrochemical reactions, catalytic reactions are usually actualized from atoms or groups of atoms which are attained to the surface. Therefore catalytic activity of the materials can be increased by metal atom doping. Pt atom and its cluster has high catalytic activity [11], for example, thin Pt layer on GaN thin films enhanced the sensitivity of the sensor to alcohol molecules [12]. Gas sensors can be utilized in combustion control and leak detection of hydrogen

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and hydrocarbon gases. There are several studies on production of such gas sensors. Pt-GaN Schottky diodes being them, are suitable for the detection of small molecules and sensing hydrogen or hydrocarbon species [13]. Over the recent years, Pt nanoparticles braced on n- and p-type doped GaN and their catalytic activity have been investigated by Stutzmann et. al. [5]. Numerous experimental and theoretical Pt-doped GaN studies have been realized using bulk or thin film forms of GaN, yet to the best of our knowledge, there is no study on Pt adsorption on GaN monolayer until now. Thus, it is important to investigate Pt-modified GaN monolayer. In this paper, we systematically examine Pt adsorption on h-GaN monolayer by varying the coverage ratio. According to our calculations, Pt atom is chemically adsorbed on top of the nitrogen site in GaN monolayer and hence can modify the electronic structure of GaN.

2. Material and Method

Our calculations are based on the first-principles spin polarized and spin unpolarized plane wave method within density functional theory (DFT) using ultrasoft pseudopotentials. The electronic configuration for the valence states are considered as: Ga: $4s^2 4p^1$, N:$2s^2 2p^3$, Pt:$5d^9 6s^1 6p^0$. The exchange-correlation functional is approximated within generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) parametrization [14]. Quantum Espresso software is used for our numerical calculations [15]. Brillouin Zone is sampled using (24×24×1) Monkhorst-Pack special k-points mesh for (1×1) GaN unit cell [16]. Kinetic energy cutoff of 476 eV (35 Ry) is used for the plane-wave basis set. Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is used to optimize the atomic positions and lattice constants [17]. The energy convergence criterion is chosen as 10^{-5} eV for two successive iteration steps, and the maximum Hellmann–Feynman forces exerted on each atom is reduced to less than 0.05 eV/Å upon ionic relaxation. We pay attention to reducing the pressure on the unit cell to less than 0.5 kbar. We chose the smearing method as Methfessel–Paxton type with a smearing width of 0.01 eV. In order to vanish the layer-layer interactions, vacuum length is taken as 20 Å. Charge transfers between the atoms are determined by Löwdin analysis [15]. In this study two supercells of the GaN monolayers are used to determine the coverage effect of Pt atom. (2×2) and (4×4) supercells of GaN monolayers are used, which are comparable with platinium coverage ratio of (θ=1/8) and (θ=1/32), respectively.

3. Results

First, (1×1) unitcell of hexagonal GaN monolayer was examined. We obtained the optimized lattice constant of the structure as a = 3.21 Å and the distance between the nearest Ga and N atoms is d = 1.85 Å, which are consistent with previous studies [18, 19]. With respect to Löwdin analysis results, N atoms take 0.87 electrons from Ga atoms, in accordance with their electronegativity difference. The cohesive energy is -11.17 eV per Ga-N pair, which is attained by subtracting the total energy of Ga and N isolated free atoms from that of the optimized GaN monolayer. GaN cohesive energy is lower than BN and AlN, in compliance with their electronegativities. In order to examine Pt adsorption, (1×1) unit cell of h-GaN monolayer was enlarged to a (2×2) supercell. A single Pt atom was placed on the GaN monolayer, and four possible adsorption sites were considered for this procedure. These sites are illustrated in Figure 1 as follows: hollow site (center of the hexagon, **H**), top site (top site of the Ga atom, $\mathbf{T_{Ga}}$ and top site of the N atom, $\mathbf{T_N}$) and bridge site (above the center of the nearest Ga-N bond, **Br**).

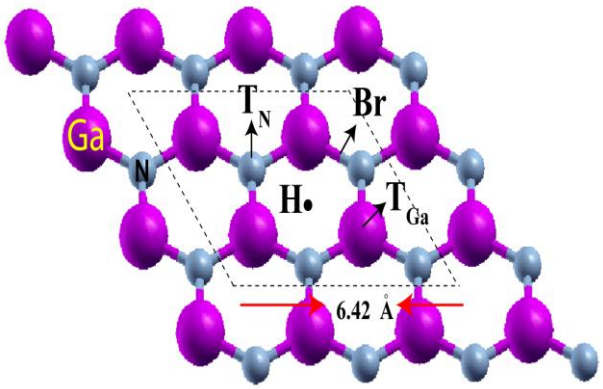

Figure 1. h-GaN monolayer. (2×2) GaN supercell with lattice constants a=b=6.42 Å is delineated by dashed lines. Possible adsorption sites are also illustrated.

After obtaining the optimized structure, adsorption energy of Pt atom on the h-GaN monolayer is calculated from the expression below;

$$E(ads)=E(GaN)+E(Pt)-E(GaN+Pt) \qquad (1)$$

where *E(GaN)* is the total energy of the bare GaN substrate, *E(Pt)* is an isolated spin-polarized platinum atom energy, and *E(GaN+Pt)* is the energy of the system of Pt adsorped to the substrate. The positive value of *E(ads)* indicates that the binding of Pt atom to GaN monolayer is favorable for a given geometry. The calculated adsorption energies for $\mathbf{T_N}$, $\mathbf{T_{Ga}}$, **Br** and **H** sites are 3.26, 1.28, 3.25 and 2.12 eV, respectively. When Pt atom is placed initially at the **Br** site, it migrates to the $\mathbf{T_N}$ site upon relaxation. Hence, both sites have similar adsorption energies. These calculations determine the $\mathbf{T_N}$ site as the energetically most favorable configuration. After the Pt atom is adsorbed on GaN monolayer, Ga-N bond lengths increase to 1.86 and 1.94 Å, and Pt atom is 2.05 Å above the N atom, while the nearest Pt-Ga distance is 2.62 Å. Therefore, the lattice constants of (2×2) GaN monolayer become 6.49 Å.

The electronic structure of bare and Pt adsorbed (2×2) GaN monolayers are illustrated in Figure 2. As

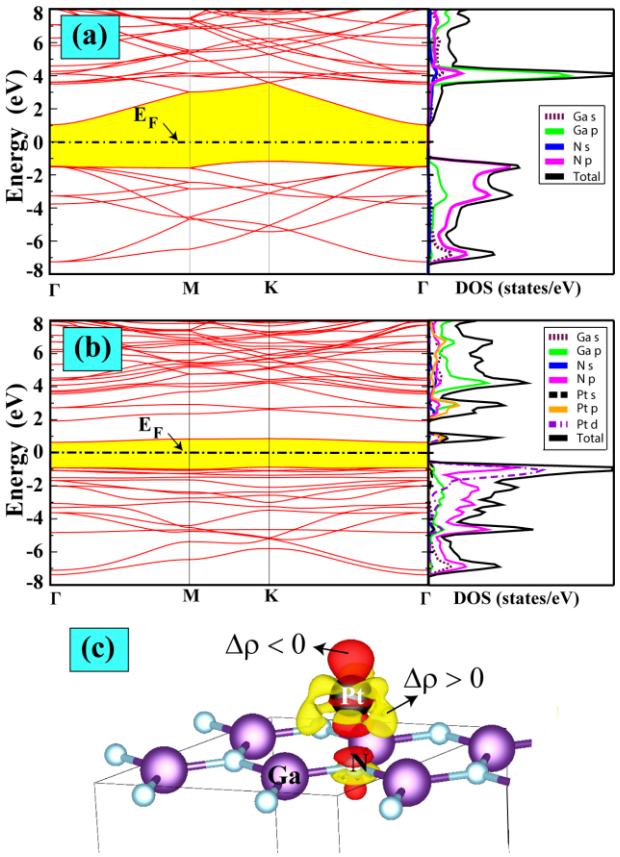

Figure 2. (a) Electronic band structure of bare (2×2) GaN monolayer, the electronic partial density of states are given in the right panel. (b) Electronic band structure of Pt adsorbed (2×2) GaN monolayer for the most favorable configuration, the electronic partial density of states are given in the right panel. (c) Charge density isosurfaces are shown. Red depicts the depletion of charge, while yellow is for accumulation.

seen in Figure 2 (a), bare GaN monolayer has a 2.1 eV indirect band gap between the Γ to K high symmetry points. This value is consistent with a previous study [19]. As evident in Figure 2 (a), valence band maximum in GaN is dominated by N 2*p* orbitals where slight contribution comes from Ga 4*p* states. Ga 4*s* states are also weaker and located at somewhat lower energies. On the contrary to valence bands, Ga 4*p* orbitals have the highest intensity at the conduction band around 4 eV. After Pt atom is adsorbed at $\mathbf{T_N}$ site, the electronic structure of GaN monolayer is significantly changed (please, see Figure 2 (b)). According to the Löwdin analysis, 0.22 electrons transfer from N atom (under Pt) to Pt atom. Pt adsorption can reduce the degeneration in GaN electronic band structure at the valence band maximum, and there occurs N *p* – Pt *d* hybridization around -1 eV. While there is a localize state of Pt atom in the vicinity of 0.6 eV, Pt *p*, and Ga *p* orbitals dominate the bands in the range of 2-3 eV. With these interactions, band gap reduces in GaN monolayer to 1.3 eV. This band gap energy value is very suitable for optical devices, that operate in the visible region.

Finally, GaN monolayer was enlarged to a (4×4) supercell for reducing the interaction of Pt atoms between the successive cells. This way, Pt atom can mimic the isolated adatom, thereby the diffusion energy barrier of Pt atom on GaN monolayer can be determined. Variation of the energy difference versus the Pt atom position on GaN is illustrated in Figure 3. These energies are obtained by single point energy calculations. Zero of energy is set to the adsorption energy of Pt atom when it is on the **Br** site. Pt atom was observed not to be adsorbed on the **Br** site, contrarily to the (2×2) GaN supercell. The atomic position of Pt atom is fixed on **Br** site in order to calculate its binding energy. As seen in Figure 3, Pt atom needs a drastic energy to migrate from $\mathbf{T_N}$ site to other adsorption sites. This implies that when single Pt atoms are sent successively to the GaN surface, they bind only to the N atoms. For confirming this case, two Pt atoms were initially placed on two separated Ga atoms, where after the relaxation both Pt atoms moved towards N atoms' top and were adsorbed therein. Similar results are obtained for oxygen binding in GaN sheets. Experimental and theoretical findings show that the oxygen binds only to the Ga atoms, and there has not been observed any oxygen on N atoms site [5, 20].

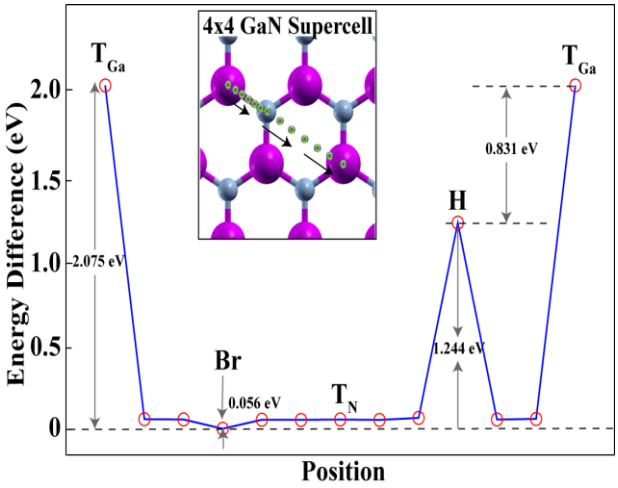

Figure 3. Diffusion of Pt atom on (4×4) GaN monolayer. Green dots show Pt position on GaN and arrows show the diffusion path.

4. Discussion and Conclusion

In summary, using first-principles plane-wave calculations carried out within the framework of DFT, the Pt adsorption on GaN monolayer is examined and it was found that Pt is chemically adsorbed on GaN monolayer on the top site of nitrogen atoms. Diffusion path calculations put forward that successively sent Pt atoms may bind only on $\mathbf{T_N}$ site of GaN sheet. Pt adsorption reduces the band gap of GaN from 2.1 eV to 1.3 eV and this gap is very suitable for optical devices which operate in the visible region. Recently, two-dimensional GaN monolayer was synthesized via graphene encapsulation [21], thus, current theoretical study may pave the way to further investigations on coating GaN monolayer by Pt atoms.

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