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# AlN and GaN single-, double-walled and alloy nitride nanotubes as an ammonia gas sensor

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## Abstract

The ammonia in the gas phase became a health human problem due to its high toxicity and for causing serious diseases, such as XXX. For this reason, the use of ammonia sensors with high sensibility is necessary for rapid detection and for the necessary measures to be taken on time. In this sense, the nanostructures, in special, nanotubes, can be used as an ammonia sensor, once its size is very reduced and the surface area available to the gas detection is broad. Besides that, the functionalized nanotubes can be modulated to be more sensitive to a specific gas. In this sense, the Density Functional Theory was applied to investigate the aluminum and gallium nitride nanotubes and its alloys to the ammonia detection. The adsorption energies and the changes in the electronic properties were crucial to evaluate the sensibility and interaction between the ammonia molecule and the nanotubes. It was found that ammonia adsorbed preferentially in the external wall nanotube, in the axial-cation. The adsorption energies, bond critical points, and the charge transfers showed that the physisorption occurs and the detection is intense in the AlN nanotubes and on the Al wall in the alloy nanotubes. The detection and sensibility increase in the alloy nanotube, which makes Ga<sub>0.5</sub>Al<sub>0.5</sub>N a great candidate for an ammonia sensor.

**Keywords:** Alloy nanotube; DFT; ammonia; gas sensor.

## 1. Introduction

### OLHAR ARTIGOS DA PASTA BIBLIOGRAFIA

Diferentes materiais que são sensores de NH<sub>3</sub>.

Falar de AlN e GaN como sensores de NH<sub>3</sub>.

Ver se tem algum artigo de heteroestrutura AlN/GaN (ou outra) que foi usada ou testada como sensor de NH<sub>3</sub> (pq eu pesquisei e não encontrei).

Falar do pq é bom a heteroestrutura e, em especial, nanotubo.

The ammonia (NH<sub>3</sub>) is widely used in many areas, such as food technology, chemical engineering, medical diagnosis, automotive fuels, and others [REF]. For this reason, the atmospheric NH<sub>3</sub> is convenient not only by industry, but also from agriculture, combustion of chemical plants and motors, and by organic materials decomposition [REF]. However, despite being a common atmospheric gas, the NH<sub>3</sub> is toxic and it is colorless turns it more dangerous. According to the National Institute for Occupational Safety and Health, 500 ppm of NH<sub>3</sub> is dangerous to life and health, and 15 minutes of exposure corresponds to 35 ppm [REF]. In this sense, its detection can be time-consuming, especially in the industry.

Many materials were proposed as an ammonia sensor, however, many times, the sensor does not have a great ammonia sensibility, the cover molecules detection needs to be high for detection to occur, and the device sensor can be wide. **LISTAR OS MATERIAIS.**

As stated, the chemical bonds formed by the heterostructures significantly change the properties in comparison to that of the original material. In this sense, Al<sub>0.5</sub>Ga<sub>0.5</sub>N and Ga<sub>0.5</sub>Al<sub>0.5</sub>N nanotubes were theoretically analyzed as an ammonia sensor and compared with single- and double-walled AlN and GaN nanotubes. Changes in the band gap, band structure, atomic charges, new levels on the density of states, associate with adsorption energy, were investigated to help to predict the use of the nitride nanotubes as an ammonia gas sensor. Besides, this work also aims to contribute to the advancement in the research of the application of nitride nanotubes, as well as the research of ammonia sensors.

## 2. Computational method

Periodic computational simulations using Density Functional Theory (DFT) with the B3LYP[1] hybrid functional were made by using the CRYSTAL17 package[2]. The aluminum, gallium, nitrogen, and hydrogen atomic centers were described by 86-21G\*[3], 86-4111d41G[4], 6-21G\*[5] and 5-11G\*[6] all-electron basis sets, respectively. The functional, basis set and accuracy methodology choice are based on the results of previously published research.[7,8]

The following step-by-step strategy has been adopted to simulate NH<sub>3</sub> adsorption on nitride nanotubes. The computational nanotube models were defined from a previous study of our group.[7][XXX] First, the nanotubes were obtained from the (0001) surface with one and two layers of AlN (or GaN), of wurtzite bulk structure, and rolled-up to the armchair single-walled (SWNT) and double-walled (DWNT) nanotubes with 20 Å of diameter. These structures were designed as an ideal model to perform adsorption studies thanks to its minimum energy strain. The alloy nanotube models were constructed by the substitution of Ga by Al atom onto the DWAlNNT, thus forming Al<sub>0.5</sub>Ga<sub>0.5</sub>N or Ga<sub>0.5</sub>Al<sub>0.5</sub>N.

In DFT simulation, in the absence of any dynamic and thermal effects, the final configuration of adsorbate is significantly influenced by its initial position. In order to explore all the possibilities and to individuate the adsorption sites, several different starting configurations were investigated. In this sense, four adsorption sites were considered on the armchair nanotube: the axial and equatorial positions of Al (Ga) and N atoms. It is noteworthy that in the alloy nanotubes it was also evaluating the influence of the difference between the internal/external material. For each adsorption site, two different molecular approaches were performed: via nitrogen and the hydrogen atom. Also, it was investigating the adsorption in the cavity of the nanotube.

The adsorption energy was calculated according to the expression:  $E_{ads} = E_{NT+NH_3} - E_{NT} + E_{NH_3} + E_{BSSE}$ ; where  $E_{NT+NH_3}$  is the total energy of the optimized nanotube with adsorbed NH<sub>3</sub> molecule,  $E_{NT}$  is the total energy of the isolated optimized nanotube,  $E_{NH_3}$  is the total energy of ammonia in the gas phase, and  $E_{BSSE}$  is the correction energy due to the basis set superposition error (BSSE).[9] In this work, the *posteriori* counterpoise method correction was applied to all the

energies as  $EBSSSE = ENT_{frozen} - ENT_{ghost} + (ENH3_{frozen} - ENH3_{ghost})$ ; where all the energies refer to the geometries of the two separated parts “frozen” in the minimum adsorption configuration (final optimization structure), with and without ghost functions, respectively.

Finally, the electronic properties of the pure nitride nanotubes and the adsorbed nitride nanotubes were evaluated and compared, which helped to predict the kind of adsorption and to measure the potential application of the nanotube as ammonia sensor. Also, the NT–NH<sub>3</sub> interactions were characterized by exploiting the potentiality of Bader topological analysis of the electron density, as implemented in the TOPOND program[10] incorporated in the CRYSTAL package. A complete search of the bond critical points (BCP) between the adsorbates and the nanotubes has been carried out, and their topology has been fully characterized to clarify the bonding nature.

### 3. Results and Discussion

The preliminary investigation on the different sites confirmed that NH<sub>3</sub> adsorption takes place via nitrogen on the cation in the axial position. Besides, it was found great difference energy into adsorption when occurs in the cavity and the external surface of the nanotubes. The difference found between the adsorption in the inner and outer wall covers a range from 0.30 kJ.mol<sup>-1</sup> to 35.17 kJ.mol<sup>-1</sup> (for DWGaN and Ga<sub>0.5</sub>Al<sub>0.5</sub>N nanotubes, respectively) and indicates that the lowest energy refers to adsorption on the outer wall of nanotubes (see Figure S1 and Table S1). It was also evaluated the possibility of the ammonia molecule dissociation into H and NH<sub>2</sub>, and it was confirmed that in all cases the dissociation did not occur.

Once that the periodic methodology is employed, all the configurations represent the adsorption of an infinite row of NH<sub>3</sub> molecule along the nanotube x-direction, which corresponds to 1 NH<sub>3</sub> per unit cell. However, to measure the influence of the ammonia interaction in the infinite periodic row, the single-molecule dilution limit was evaluated taking to account a supercell calculation and only 1 NH<sub>3</sub> molecule. It was found that the row of NH<sub>3</sub> in the periodic model leads to a stabilization of the NH<sub>3</sub> adsorption, and the supercell models have almost 10% higher energy than the models with 1-row of NH<sub>3</sub> molecule. In this sense, only the periodic 1-row NH<sub>3</sub> adsorption models were analyzed.

After, the geometry parameters, the distortion, adsorption, and band gap energies were measured taking to account the minimal adsorption structures discussed before.

The results are summarized in Table 1 and were compared with the bare nanotubes values.

Table 1: Al(Ga)-N, N<sub>NH3</sub>-H, and Al(Ga)-N<sub>NH3</sub> bond lengths (Å), nanotube ( $\alpha_{NT}$ ) and NH<sub>3</sub> ( $\alpha_{NH3}$ ) bond angles (degree), distortion ( $E_{dist}$ ) and adsorption energies ( $E_{ads}$ ) in kJ/mol and band gap ( $E_{gap}$ , eV) of NH<sub>3</sub>@NT. The sub-index  $s$  refers to the atoms of the adsorption site.

Nanotube	$d_{Al(Ga)-N}$	$d_{s(Al(Ga)-N)}$	$\alpha_{NT}$	$\alpha_{sNT}$	$d_{Al(Ga)-N}$	$d_{NNH3-H}$	$\alpha_{NH3}$	$E_{dist}$	$E_{ads}$	$E_{ads} + E_{BSSE}$	$E_{gap}$
AlN	1.79	1.79	120	120	-	-	-	-	-	-	6.59
GaN	1.84	1.84	120	120	-	-	-	-	-	-	4.73
DWAlN	1.90	1.85	116	120	-	-	-	-	-	-	5.94
DWGaN	1.98	2.15	115	122	-	-	-	-	-	-	3.62
Al <sub>0.5</sub> Ga <sub>0.5</sub> N	1.92	1.97	116	122	-	-	-	-	-	-	4.28
Ga <sub>0.5</sub> Al <sub>0.5</sub> N	1.93	2.01	116	121	-	-	-	-	-	-	4.96
NH <sub>3</sub> @AlN	1.79	1.82	120	118	2.30	1.02	107	2.95	-18.86	-5.44	4.75
NH <sub>3</sub> @GaN	1.86	1.91	116	121	2.47	1.09	107	1.23	-17.78	-4.64	4.61
NH <sub>3</sub> @DWAlN	1.90	2.03	116	121	2.24	1.02	108	3.73	-19.84	-6.31	4.88
NH <sub>3</sub> @DWGaN	2.04	1.95	116	122	2.40	1.02	107	1.91	-19.44	-5.21	3.41
NH <sub>3</sub> @Al <sub>0.5</sub> Ga <sub>0.5</sub> N	1.92	2.00	115	123	2.51	1.02	107	1.34	-17.64	-5.46	4.14
NH <sub>3</sub> @Ga <sub>0.5</sub> Al <sub>0.5</sub> N	1.94	2.25	115	123	2.16	1.04	109	35.61	-22.63	-7.35	4.55

According to Table 01, the nitrogen atom of ammonia interacts with the nanotubes cation in a distance that varies from 2.16 to 2.51 Å. In all cases, the ammonia distorts the nanotube structures, the bond distance and angles have a little distortion in the atoms of the adsorption sites. However, the NH<sub>3</sub> molecule did not suffer a great distortion in its structure.

It was found a great influence of the BSSE calculated in all the adsorption energies due to the interaction between the H of ammonia molecule and the nitrogen of the nanotubes. The BSSE energies lead to a decrease of almost 16 kJ.mol<sup>-1</sup> in the adsorption energies and show the importance to evaluate the influence of the basis set superposition in the adsorption calculations using DFT, that if neglected would yield results and incorrect conclusions. With the BSSE correction, the adsorption energies vary from -4.64 to -7.35 kJ.mol<sup>-1</sup>, being the models with minor  $E_{ads}$  the Al<sub>0.5</sub>Ga<sub>0.5</sub>N and DWGaN. Anyway, evaluating the adsorption based only on the adsorption energy, we can say that the adsorption is possible to occur in all the nanotubes analyzed. Nonetheless, to see if occurs the effective adsorption in all models, other analyzes are required.

The topological analysis of the electron density was performed, in special, to the atoms involved in the NT–NH<sub>3</sub> interaction, the results are reported in Table 2. The bond critical points (BCPs) found in the Al-N and Ga-N bonds of the nanotubes have, on average,  $\rho=0.09$ ,  $\nabla\rho^2=0.37$ ,  $H\rho=-0.25$  and  $|V|/G=1.23$ , which suggests a transition character of their bonds, i.e., neither ionic either covalent. In all models, it was found a BCP between the cation of the nanotube and the nitrogen atom of the NH<sub>3</sub> molecule, which confirmed the interaction NTs-NH<sub>3</sub>. The analyzes of the BCPs suggest also a transition character of the bond, although the properties showed a tendency to an electrostatic interaction between NH<sub>3</sub> and nanotubes. The critical points are closer to the Al(Ga) atoms, and the charge analyzes of these atoms showed an electronic charge transition from the cation to the nitrogen atom for the NH<sub>3</sub> molecules. In contrast, a not appreciable charge transfer is observed between the nanotube atoms, they keep both their volume and charge after the adsorption. No critical point was found between the hydrogens atoms of the NH<sub>3</sub> and the nanotube atoms.

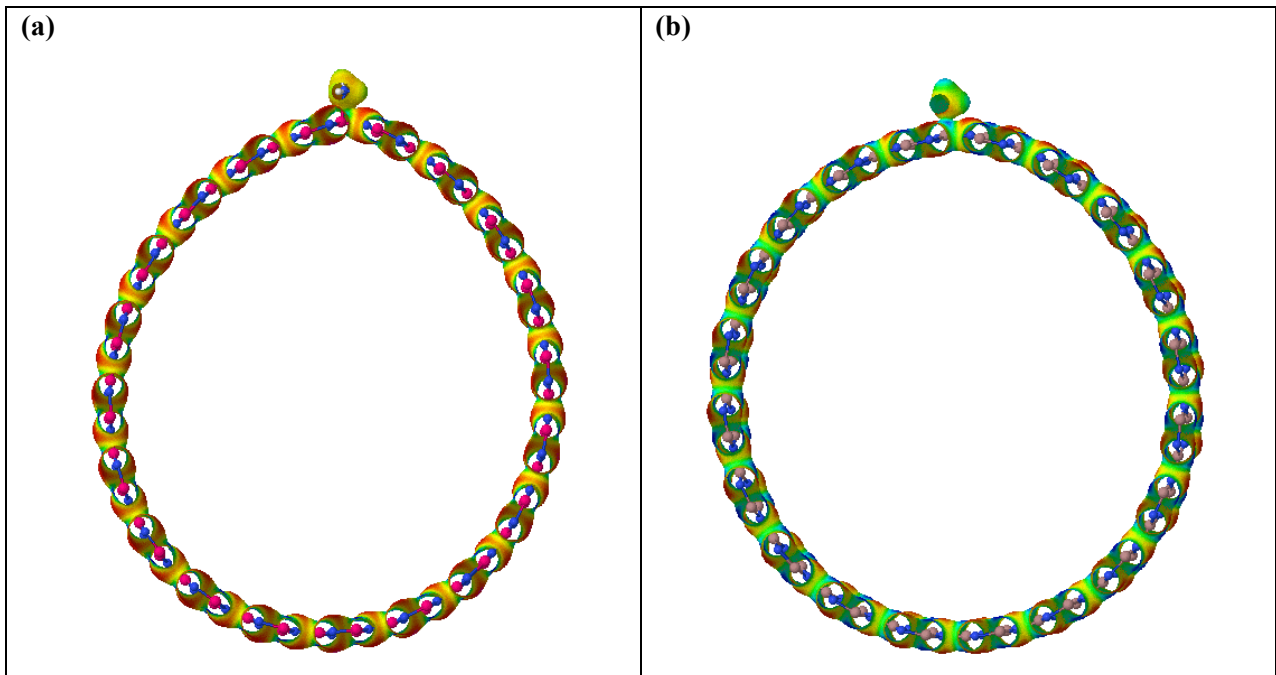
As discussed in our previous article [REF], the single and double-walled nanotubes have a negative charge more pronounced around N atoms in the GaN nanotubes, which corresponding to a greater positive net charge on the Ga atoms than that on Al atoms. In the alloy nanotubes, the charge flows from Al to N direction, the nitrogen atom becomes more negative and the electron density is higher around the Al-N bond. In this sense, it was expected that molecules that tend to withdraw electron density, being adsorbed preferentially in the AlN nanotube or the AlN wall. In fact, the AlN and the Ga<sub>0.5</sub>Al<sub>0.5</sub>N nanotubes showed a better interaction with the NH<sub>3</sub> molecules, and have the smaller  $E_{ads}$  and the higher nanotube distortion, due to the interaction. This strong interaction is also confirmed by the greater charge transfer from the Al atoms of the nanotubes to the N atom for NH<sub>3</sub> molecules.

Table 2: Distance of Al(Ga) and N of NH<sub>3</sub> atoms to bond critical points ( $d_{BCP}$ , Å), and several topological properties electron charge density ( $\rho$ ), its Laplacian ( $\nabla^2\rho$ ), the  $|V|/G$  ratio, and the bond degree ( $H/\rho(r)$ ) and ellipticity ( $\epsilon$ ), all in atomic units

	$d_{BCP-Al(Ga)s}$	$d_{BCP-N(NH_3)}$	$\rho$	$\nabla^2\rho$	$ V /G$	$H/\rho(r)$	$\epsilon$
<b>NH<sub>3</sub>@AlN</b>	0.919	1.378	0.029	0.096	1.134	-0.130	0.188
<b>NH<sub>3</sub>@GaN</b>	0.895	1.344	0.034	0.113	1.161	-0.161	0.127

<b>NH<sub>3</sub>@DWAIN</b>	1.228	1.339	0.025	0.066	1.130	-0.099	0.096
<b>NH<sub>3</sub>@DWGaN</b>	1.143	1.259	0.036	0.086	1.236	-0.183	0.056
<b>NH<sub>3</sub>@Al<sub>0.5</sub>Ga<sub>0.5</sub>N</b>	1.197	1.311	0.029	0.071	1.185	-0.139	0.077
<b>NH<sub>3</sub>@Ga<sub>0.5</sub>Al<sub>0.5</sub>N</b>	0.867	1.291	0.041	0.144	1.170	-0.178	0.068

To verify the charge transfer process, the charge distribution on the isodensity surface based on the electronic charge density and the electrostatic potential of nanotubes, focus in the adsorption site, is depicted in Figure 2, with isolines being drawn at increments of  $0.001 |e|/\text{\AA}$ . Comparing with the bare nanotubes, it is seen that in single- and double-walled nanotubes the uniformed charge distribution is altered by the NH<sub>3</sub> adsorption. It can be seen the charge transfer between the Al(Ga) atoms to the N atom of the NH<sub>3</sub> molecule by the positive charge localized at the Al(Ga) site and the negative charge in the N atom. A small charge transfer was observed between the hydrogen atom of the NH<sub>3</sub> molecule and the nitrogen of the nanotube surface, the hydrogen turns softly more positive by two reasons: the charge transfers for the nitrogen direct bonded (NH<sub>3</sub>) and the transfer for the nitrogen of the nanotube. This behavior is also observed in the alloy nanotubes, however, in the Ga<sub>0.5</sub>Al<sub>0.5</sub>N nanotube, the charge transfer is a little higher. In both alloys, the cation becomes more positive after the adsorption, although in the AlN wall the charge transfer is more effective due to the greater interaction with the NH<sub>3</sub> molecules, as observed in the AlN nanotubes.





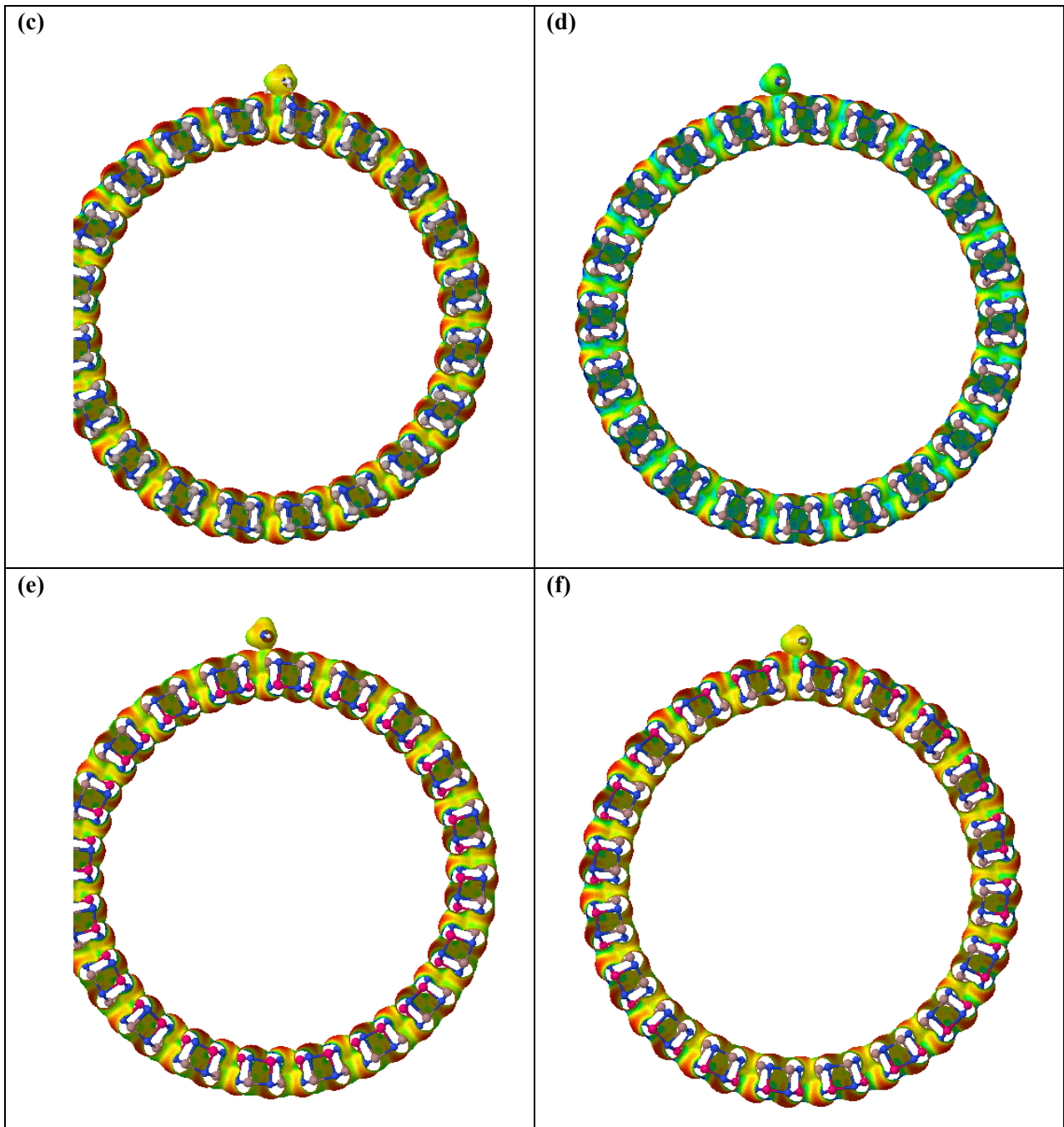
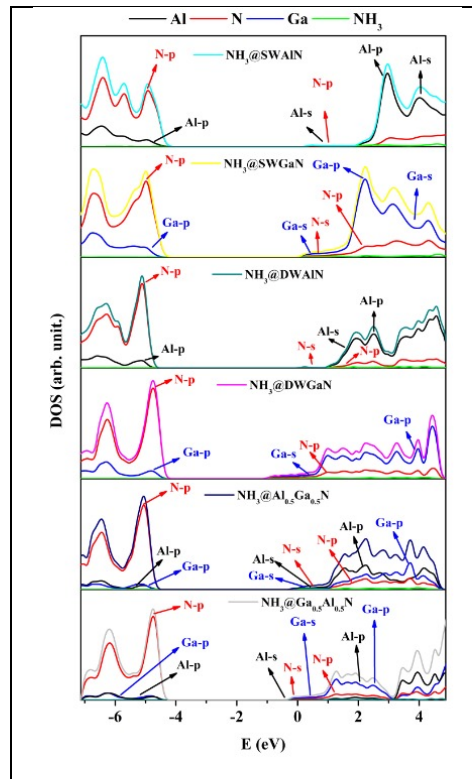


Figure 2: Charge distribution on the isodensity surface of (a)  $\text{NH}_3@ \text{AlN}$ , (b)  $\text{NH}_3@ \text{GaN}$ , (c)  $\text{NH}_3@ \text{DWALN}$ , (d)  $\text{NH}_3@ \text{DWGaN}$ , (e)  $\text{NH}_3@ \text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$  and (f)  $\text{NH}_3@ \text{Ga}_{0.5}\text{Al}_{0.5}\text{N}$  nanotubes.

The  $\text{NH}_3$  adsorption changes the band gap of all systems. However, the AlN nanotubes suffered the highest decrease in their band gaps after the adsorption, -1.06 eV and -1.84 eV, for  $\text{NH}_3@ \text{AlN}$  and  $\text{NH}_3@ \text{DWAIN}$ , followed by the  $\text{Ga}_{0.5}\text{Al}_{0.5}\text{N}$ , that decrease -0.37 eV. For the other models, the decrease is almost -0.14 eV. The changes in the electronic properties were also observed in the band structures and density of

states (DOS). Despite the minimum contribution in the DOS (Figure 3) in both valence and conduction bands, the  $\text{NH}_3$  molecules change substantially the behavior of the nanotubes in the range analyzed, in special, in the band gap region. In a general way, the orbitals of atoms that were the most contributor before the adsorption is maintained after the adsorption. Therefore, the 2p orbitals of the nitrogen atoms are the most contributor in the valence band and near to the band gap region, while the s orbitals of the gallium and aluminum atoms are the most contributor in the conduction band.



**Figure 3:** Density of states of  $\text{NH}_3$  adsorption on analyzed nanotube models (a) SWAIN, (b) SWGaN, (c) DWAIN, (d) DWGaN, (e)  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$  and (f)  $\text{Ga}_{0.5}\text{Al}_{0.5}\text{N}$

#### 4. Conclusions

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