Ab initio study of optical properties of the [0001] Ti-surface with a carbon layer coverage and of graphene with an extensive Ti coverage

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Abstract. We used first-principles molecular dynamics at atmospheric pressure and 300 K to simulate a graphene layer, a titanium slab, the high coverage of the graphene layer with titanium, and the masking of the titanium surface with a carbon layer. The calculations were performed using the Quantum Espresso code with the GGA approximation. We then calculated the energy band structure and the optical absorption and reflectivity of the decorated surfaces. We found significant changes in these properties.

1. Introduction

Graphene and titanium have attracted scientific interest in the last decades. Graphene has extraordinary properties and a very wide gamma of applications. On the other hand, the chemistry of titanium surfaces has been studied, from experimental and theoretical approaches [1-8]. The interaction of molecules and the [0001] titanium surface has been investigated experimentally with remarkable clarity with different techniques, due to the high symmetry.

In this work, we are interested in the optical absorption and reflectivity of two surfaces that involve titanium and graphene. The first is a graphene layer with a high titanium coverage [9]. The second is the [0001] titanium surface covered with a layer of carbon [10].

We performed first principles, molecular dynamics calculations to optimize each one of these systems. Then, within the random phase approximation, we calculated the dielectric tensor and obtained the absorption and the reflectivity. We found these optical properties for pristine graphene, the [0001] titanium surface, graphene with a high titanium coverage, and the [0001] titanium surface masked with a carbon layer. We make a comparison with the values in the literature and show the changes we predict in the absorption and reflectivity of graphene and the [0001] titanium surface.

2. Method

We used the Quantum Espresso code [11] to perform numerical simulations. The density functional theory was considered to do first-principles molecular dynamics optimizations at atmospheric pressure and 300K of the surfaces we have discussed.

We utilized The Troullier-Martins norm-conserving pseudopotentials [12], in the separable form given
by Kleinman-Bylander [13]. We also used the Perdew-Burke-Ernzerhof (PBE) approximation for GGA [14]. We performed non-relativistic and non-spin polarized calculations.

We used the Monkhorst–Pack particular k point scheme [15] and took 40 k points. Cut-off energy of 1100 eV was considered, with the threshold energy for convergence of 1.0 X 10^-7 eV.

We validated the selected pseudopotentials by performing calculations of the titanium and graphene lattice parameters by minimizing the energy. We obtained for titanium a = 2.863 Å, and c = 4.5444 Å. The experimental values are 2.950 Å and 4.683 Å, respectively. For the graphene layer, we got 1.42 Å, and the experimental value is 1.42 Å [16].

To obtain the titanium surface, we considered a hexagonal unit cell, with a = b = 5.0 Å and c = 40 Å, with periodic conditions, containing the four layers of atoms. The value of c is large enough to avoid non-convenient interactions. After optimization, we performed a molecular dynamics calculation at atmospheric pressure and 300 K [10].

For the optimization energy of the carbon layer on the [0001] titanium surface, we followed [10] and obtained for the adsorption energy -2.054 eV per carbon atom.

The optical properties, the absorption, and the reflectivity were calculated from the complex dielectric function. We obtained the imaginary component of the dielectric tensor from the structure of electronic bands in the limit of the linear optics. Within the random phase approximation (RPA) [17],

\[
Im \varepsilon_{\alpha\beta}(\omega) = \frac{4\pi^2}{m^2\omega^2} \sum_{\mathbf{k},\mathbf{p}} \langle c_{\mathbf{k}} | p^{\alpha} | v_{\mathbf{p}} \rangle \langle v_{\mathbf{p}} | p^{\beta} | c_{\mathbf{k}} \rangle \delta(\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} - \omega) \tag{1}
\]

In equation (1), \(Im \varepsilon_{\alpha\beta}\) is the imaginary part of the dielectric tensor. The wave functions corresponding to the conduction and the valance bands with crystal wave vector \(\mathbf{k}\) are \(c_{\mathbf{k}}\) and \(v_{\mathbf{k}}\), and \(p\) is the momentum matrix element between states of energy bands \(\alpha\) and \(\beta\) with crystal momentum \(\mathbf{k}\).

From (1) by the Kramers-Kronig relations [18]

\[
Re \varepsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \frac{2}{\pi} \int_0^\infty \frac{\omega Im \varepsilon_{\alpha\beta}(\omega)}{\omega^2 - \omega'^2} d\omega' \tag{2}
\]

The reflectivity at normal incidence \(R_\alpha\) is:

\[
R_\alpha(\omega) = \left(\frac{n+1}{n-1}\right)^2 + \left(\frac{k}{n+1}\right)^2 \tag{3}
\]

Where \(n\) and \(k\) are the refractive index and extinction coefficient respectively, as given in (4) and (5)

\[
n_{\alpha\alpha} = \sqrt{\frac{|E_{\alpha\alpha}(\omega)| + Re E_{\alpha\alpha}(\omega)}{2}} \tag{4}
\]

\[
k_{\alpha\alpha} = \sqrt{\frac{|E_{\alpha\alpha}(\omega)| - Re E_{\alpha\alpha}(\omega)}{2}} \tag{5}
\]

3. Results and discussion

When we achieved all the optimizations, we calculated the optical properties, absorption, and reflectivity of each system. We calculated the complex dielectric tensor for each one within an energy range of 0-40 eV.

3.1. Optical properties of Ti
In Figure 1, we show the calculated absorption and reflectivity for pure titanium. The results are in good agreement with those reported in [18]. Notice that in titanium’s absorption, there are two prominent peaks. One is at around 5 eV and the other about 36 eV. Within 12 eV and 32 eV, the absorption is close to zero.

In the reflectivity, we have a value near 1 in the infrared region and drops fastly to a minimum located around 0.7 eV. It grows up quickly to near 1, at around 8 eV. Then, it decreases slowly up to approximately 11 eV and diminishes fastly to close zero at about 18 eV. Finally, a peak appears at around 37 eV. The increase is rapid after 30 eV.

3.2. Optical properties of the Ti-carbon layer
In figure 2, we present the optical properties of titanium with a carbon layer coverage. We can see in this figure that the absorption has only a maximum value at around 4 eV. Then, it decreases to almost zero at approximately 9 V. It grows up a bit to a small maximum at about 10.2 eV and then exponentially goes to zero. There are significant changes concerning pure titanium.

Notice that the reflectivity, at low energies, has a value of around 0.8. It decreases to a minimum of 0.6 approximately, at about 1.0 eV. Roughly it maintains this value up to 2.1 eV. Then, it falls to a minimum of 0.55. This minimum is at around 3.5 eV. Then, it grows up to a maximum of 0.7 at about 5.8 eV. Afterward, it drops quickly to zero at approximately 12 eV and remains at that value. We found substantial changes from titanium reflectivity.

3.3. Optical properties pristine graphene
In figure 3, we also show the reflectivity and absorption of the pristine graphene [19]. In this case, the absorption is close to zero everywhere except at around 11 eV and 15.5 eV, where it shows two maxima. The reflectivity shows two peaks, one located around 11 eV, and the other (which is slightly larger) at about 22 eV.

3.4. Optical properties of graphene with a high titanium coverage
In figure 4, we present the optical properties of graphene with high titanium coverage. In this figure, we can see that the absorption shows three peaks. The first, the smallest, is located around 2 eV. The second, located at about 5 eV, is a bit larger. There is a minimum situated at around 4 eV. The third peak, and the largest, is located at about 33 eV. We obtained significant changes concerning pristine graphene.

We can notice in the reflectivity, two maximum values, and a minimum between them, the first maximum located at about 1.9 eV. The second is situated at around 5.8 eV. The minimum occurs at about 3.9 eV. Afterward, the reflectivity is close to zero, except for a tiny peak located at approximately 35 eV. There are significant changes concerning pristine graphene.
4. Conclusions
We found substantial changes in the optical properties of graphene when decorated with a high titanium coverage. For absorption, instead of the two absorption peaks in the ultraviolet region, one maximum appears at a larger frequency. Furthermore, two maxima show in the infrared and visible ranges. In the case of the reflectivity, the two humps, located in the ultraviolet zone, disappear. Two peaks appear at smaller frequencies in the infrared and visible regions.

We found significant differences in the optical properties of titanium after the decoration with the carbon layer. The absorption peak at around 35 eV disappears. The other maximum at about 5 eV gets larger and slimmer but stays at the same position approximately. The reflectivity loses its peak at large frequencies. The step at around 12 eV moves to 6.5 eV roughly. The maximum value decreases from about 9 eV to approximately 7 eV.

Acknowledgments
We thank Dirección General de Asuntos del Personal Académico de la Universidad Nacional Autónoma de México, partial financial support by Grant IN113220. We also appreciate UNAM-Miztli-Super-Computing Center technical assistance by the project LANCAD-UNAM-DGTC-030.

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