Changes in the reflectivity of a lithium niobate crystal decorated with a graphene layer

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Abstract. Density functional theory and molecular dynamics were used to study the interaction of a graphene layer with the surface of lithium niobate. The simulations were performed at atmospheric pressure and 300K. We found that the graphene layer is physisorbed with an adsorption energy of -0.8205 eV/C-atom. Subsequently, the optical absorption of the graphene-(lithium niobate) system was calculated and compared with that of graphene solo and lithium niobate alone, respectively. The calculations were performed using the Quantum Espresso code with the GGA approximation and Vdw-DF2 (which includes long-range correlation effects as Van der Waals interactions).

1. Introduction

The photorefractive crystals motivate a special interest because of their prominent and highly advanced applications such as holographic memories, phase conjugators, dynamic interferometry and pattern recognition among many more. Since the first publication on the explanation of their physical properties [1, 2], these materials have revolutionized and given life to many applications of nonlinear optics.

Lithium niobate (LiNbO₃) is an anisotropic crystalline material. This means that the refractive indices depend upon the direction of crystal axes. It is a photorefractive material. It is a strongly asymmetric crystal, and it can change the polarization state of the light passing through, with the variation of an electric field applied externally. This change is due to an electro-optical effect, which can be explained as follows. An external electric field applied across the crystal changes the refractive index nₑ (special) and nₒ (ordinary), according to the crystal orientation and applied field. This material is used for making modulators intensity, optical components in advanced technology and in many other devices.

The structure of LiNbO₃ belongs to the rhombohedral space group (trigonal) R3c, with a point group 3m, when it is grown under controlled temperature. For crystal growth at temperatures above the phase transition temperature (~1483 K), the crystal structure is center-symmetrical of the group R3m. There are three options in the selection of the axes of LiNbO₃ cells. The first one corresponds to the rhombohedral. The second corresponds to the hexagonal, and the last to the hexagonal-ortho hexagonal. The first two are suitable for crystallographic purposes and for determining its structure. For most applications, the preferred setting is orthogonal and tensor components give properties with respect to these axes.

The LiNbO₃ crystal (CLN) is very commercial, and is usually grown with the mixture of ([Li]/[Nb] = 48.6/51.4) by the Czochralsk method. The CLN is grown easily with a homogeneous
composition and great optical quality. However, there may be some intrinsic defects within the crystal due to lack of Li. At present, the CLN can be obtained as mono crystal with excellent quality [3].

On the other hand, graphene, a sheet of a single layer of graphite, is a semiconductor [4, 5] with a forbidden zero band which has been of great interests in theoretical and experimental studies. Graphene has unique electronic properties resulting from its hexagonal honeycomb lattice structure, which causes electrons to behave as massless relativistic fermions satisfying the Dirac equation [6]. The Hall Effect [7] has been observed in graphene. Studies have also shown that there is spin-orbit coupling in this material [8-11]. These and other unusual electronic properties of graphene make it a promising material for electronic devices. However, the lack of a band gap in graphene establishes limitations on their practical applications. It is very important to find ways to effectively tune the band gap of graphene to expand its applications in nano electronics and optoelectronics.

In this work, density functional theory and molecular dynamics were used to study the interaction of a graphene layer with the surface of lithium niobate. The simulations were performed at atmospheric pressure and 300K. Then we calculated the reflectivity of the graphene-(lithium niobate) system. For our simulations, we considered a lithium niobate slab (figure 1) with a thickness of 5.14 Å.

2. Method

The density functional theory was used, with the general gradient approximation (GGA) and Vdw-DF2 (which includes long-range correlation effects as Van der Waals interactions), and molecular dynamics (MD) within the Born-Oppenheimer approximation with the Quantum Espresso code [12]. For exchange-correlation energies, we used the Perdew-Burke-Ernzerhof (PBE) approximation for GGA [13]. We used the norm conserving Martins -Troullier and Goedecker- Hartwigsen-Hutter-Teter [14] pseudopotentials.

We considered as valence electronic states for carbon 2s2p2, for lithium: 2s1, for niobium: 4d5s2, and for oxygen: 2s2p4. We performed non-relativistic, and non-spin polarized calculations. The cut-off energy was 748 eV, and we took 50 k points within the Monkhorst-Pack scheme [15]. The threshold energy convergence was 10^-8 Ry. To validate our pseudopotentials we obtained by energy minimization, in the graphene layer, for the value of the C-C bond length 1.42 Å (the experimental values are 1.42 Å). For the lithium niobate crystal with rhombohedral unit cell, the lattice parameters were \( a = 5.4940 \) Å, \( c = 13.8625 \) Å and \( \alpha = 55.867^\circ \) (experimental values \( a = 5.494 \) Å, \( c = 13.825 \) Å, and \( \alpha=55.867^\circ \), respectively [16]).

The graphene-LiNbO\(_3\) system was represented using a hexagonal cell with \( a = 5.1479 \) Å and \( c = 39.9804 \) Å with periodic conditions. It contains eight carbon atoms, eighteen oxygen atoms, six niobium atoms, and six lithium atoms (see figure 1). In the \( c \) direction, we took a large enough separation to ensure that there is no interaction between adjacent decorated lithium niobate slabs.

The adsorption energy of the graphene layer onto the surface of lithium niobate was obtained from:

\[
\Delta E = E(\text{Graphene} - \text{LiNbO}_3) - [E(\text{graphene}) + E(\text{LiNbO}_3)]
\]

Where \( E(\text{Graphene-LiNbO}_3) \) is the energy of the final configuration; \([E(\text{Graphene}) + E(\text{LiNbO}_3)]\) is the energy of the initial system, which is the graphene alone plus the LiNbO\(_3\) crystal energy alone, with no interaction between them. It was found that graphene is physisorbed on the LiNbO\(_3\) surface, and the adsorption energy is -0.8205899 eV/(C-atom), when using GGA, and -0.8154758 eV/(C-atom) GGA when we used Vdw-DF2 (which includes long-range correlation effects as Van der Waals interactions).
After the optimization of the graphene-(LiNbO$_3$) system, we calculated the band energy structure for the new system, using the method of the modified tetrahedron Blöch for integration in the first Brillouin zone [17]. The energy gap of the LiNbO$_3$ crystal was, $E_g = 3.6$ eV (the experimental value is $E_g = 3.78$ eV [18]), the energy gap for the graphene-LiNbO$_3$ system is $E_g = 0.148$ eV.

The imaginary component of the dielectric tensor can be calculated by knowing the structure of electronic bands in the limit of the linear optics, and in the formalism of the random phase approximation (RPA) where the expression is obtained [19]:

$$\text{Im} \varepsilon_{\alpha\beta}(w) = \frac{4ne^2}{m^2w^2} \sum_{c,r} \int dk |p^0|^2 |v_c v_r| |p^\beta| \delta \left( \varepsilon_c - \varepsilon_r - w \right)$$  \hspace{1cm} (1)

The real component of the dielectric tensor is derived from the Equation (1) by the Kramers-Kronig relations [19, 20]:

$$\text{Re} \varepsilon_{\alpha\beta}(w) = \delta_{\alpha\beta} + \frac{2}{n} \int_0^\infty \frac{w'\text{Im} \varepsilon_{\alpha\beta}(w')}{w^2 - w'^2} dw'$$  \hspace{1cm} (2)

The reflectivity at normal incidence is

$$R_\alpha(w) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$  \hspace{1cm} (3)

Where $n$ and $k$ are the real and imaginary part of the complex refractive index (refractive index and extinction coefficient, respectively). The components of $n$ and $k$ are given in equations (4) and (5).

$$n_\alpha(w) = \sqrt{\varepsilon_\alpha(w) + \text{Re} \varepsilon_\alpha(w)}$$  \hspace{1cm} (4)

$$k_\alpha(w) = \sqrt{\left| \varepsilon_\alpha(w) - \text{Re} \varepsilon_\alpha(w) \right|}$$  \hspace{1cm} (5)
Results and discussion

After optimization of our system (see figure 1), we calculated the adsorption energy. We found that the graphene layer is physisorbed with an adsorption energy of -0.8205 eV per carbon atom. The result for the corresponding energy band structure is shown in figure 2. For comparison, in figure 3 we show the energy band structure of lithium niobate alone. We can see big differences from the first case. Afterwards, we calculated the complex dielectric tensor for the equilibrium configuration in an energy range of 0-30 eV (which corresponds to 0-240000 cm\(^{-1}\)).

In Figure 4, we show the resulting reflectivity for the graphene-(LiNbO\(_3\)) system. In this figure, we also show the reflectivity of the graphene alone and the corresponding one of the lithium niobate alone, for comparison.

![Graph showing reflectivity](image)

**Figure 4.** Calculated reflectivities of our system, and those of graphene alone and LiNbO\(_3\) alone.

Notice that the reflectivity of lithium niobate alone has several peaks, with the maximum around 10\(^5\) cm\(^{-1}\). After that, the reflectivity decreases with increasing energy, and then it flattens up to around 1.7X10\(^5\) cm\(^{-1}\), when the last peak appears.

On the other hand, the reflectivity of graphene also has several peaks. The first one is similar in position and in magnitude to the corresponding reflectivity of lithium niobate, a little bit before 10\(^5\) cm\(^{-1}\). The largest peak is around 1.3X10\(^5\) cm\(^{-1}\). After this peak, the graphene reflectivity goes to zero.

Finally, in the reflectivity of the lithium niobate decorated with graphene, we have a smaller variation with changes in energy, than in the two previous cases. Furthermore, the largest value of the reflectivity occurs around 0.45X10\(^5\) cm\(^{-1}\) (around 5.5 eV), in a similar position of the first peak of the reflectivity of lithium niobate. However, the maximum value of the reflectivity is about 0.14 cm\(^{-1}\). This value is 31% of the value of the reflectivity of lithium niobate at the same position. There is a small peak at around 1.6X10\(^5\) cm\(^{-1}\), where the reflectivity of lithium niobate presents a peak. However, the value of the reflectivity is 16% of the corresponding value of the reflectivity of graphene.

Clearly, the effect of the graphene layer on the reflectivity of lithium niobate is strong. Besides, the resulting reflectivity of the decorated lithium niobate crystal is also very different from the reflectivity of the graphene alone.
4. Conclusions

It was found that graphene is physisorbed on the lithium niobate surface at atmospheric pressure and 300K. There are large differences of the energy band structure of lithium niobate alone with respect to graphene - (lithium niobate).

The resulting reflectivity of lithium niobate decorated with graphene is very different from the reflectivity of graphene alone, and from single lithium niobate.

The reflectivity of the lithium niobate decorated with graphene, shows a much smaller variation with changes in energy, than any of graphene and lithium niobate decorated with graphene.

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References

[1] Kukhtarev N Kiev Semenyuk A and Nauka Dumka 1971 Radiation Physics of Nonmetallic Crystals Vol.3, Chap. 1
[2] Kukhtarev Sov N Tech. Phys. Lett., 1, 155 1975. Vinetskii V, Kukhtarev N and Semenyuk Sov A Phys. Semicond. , 6(18), 879 (1972) Vinetskii V and Kukhtarev Sov N Phys. Solid State Phys., 16, 3714 (1974).
[3] Volk T and Wöhlecke M 2008 Lithium Niobate: Defects, Photorefraction and Ferroelectric Switching. Springer series in materials science 115.
[4] Springer-Verlag, Berlin K S, Novoselov, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I and Vand Firsov A A 2004 Science 306 666
[5] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Proc. Natl. Acad. Sci. U.S.A. 102, 10451
[6] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A, 2005 Nature (London) 438 197
[7] Zhang Y B, Tan Y W, Stormer H L and Kim P 2005 Nature (London) 438 201
[8] Kane C L and Mele E J, 2005 Phys. Rev. Lett. 95 226801
[9] Huertas-Hernando D, Guinea F and Brataas A, 2006 Phys. Rev. B 74 155426
[10] Min H, Hill J E, Sinitsyn N A, Sahu B R, Kleinman L and A H MacDonald 2006 Phys. Rev. B 74, 165310
[11] Yao Y, Ye F, Qi X L, Zhang S C and Fang Z. 2005 Phys. Rev. B 75 041401(R)
[12] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti, Cococcioni L M J 2009 Phys. Condens. Matter 21 395502.
[13] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865.
[14] Troullier N, Martins J L and Perdew J P 1993 Phys. Rev. B 43.
[15] Monkhorst H J and Pack J D 1976 Phys. Rev. B. 13 5188.
[16] Weis R S and Gaylord T K Lithium Niobate: Summary of Physical Properties and Crystal Structure USA School of Electrical Engineering, Georgia Institute of Technology, Atlanta, GA 30332
[17] Blöchl, Jepsen P E and O. & Andersen OK 1994 Improved tetrahedron method for Brillouin-zone integrations. Phys. Rev. B 49(23), 16223-33.
[18] Dhar A and Mansingh A 1976 J. Appl. Phys. 68 5804.
[19] Bohm, D. & Pines and A 1953 Collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas. Phys. Rev. 92(3), 609-625.
[20] Kittel and C 1966 Introduction to Solid State Phys. 3rd edition. New York, John Wiley p 648