Relazione scietifica dell'attività svolta alla Molecular Foundry (Lawrence Berkeley Laboratory, Berkeley, CA) nell'ambito di un progetto di Breve Mobilità promosso dal Consiglio Nazionale delle Ricerche.

Titolo del Programma:
Studio delle proprietà elettroniche di nanostrutture in Nitruro di Indio per applicazioni in celle Fotovoltaiche di terza generazione.

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1. Introduction and Motivation

In the last decades Indium Nitride (InN) has deserved great attention due to its outstanding electronic properties, which make it an optimal material for applications in optoelectronics and new generation photovoltaic (PV) devices. Indeed, InN has a direct band gap of about 0.7 eV and an absorption coefficient of 7×10^{3} cm^{-1} at 0.75 eV. The InN mobility and saturation velocities are high, due to the low effective mass, 0.066 m_0. Furthermore, when alloyed with Gallium, InN optical absorption changes from IR to UV light, thus it would allow one to exploit the entire visible range for PV energy production [1].
Recent interest in InN is also related to seemingly conflicting results on its observed bang gap (E_g): there have been repeated observations of an effective band gap of about 0.7 eV by optical techniques [2-3], in contrast to the value of 1.9 established for the last 20 years [4]. As for theoretical results, Density Functional Theory (DFT - both LDA and GGA calculations) was found to give rise to negative energy gaps between 0.0 and -0.3 eV [5]. In this respect, quasi-particle corrections (within the GW approximation) proved to be fundamental in predicting gap opening and correcting the electronic properties of InN, giving rise to an E_g of about 0.8 eV [6]. Indeed, despite the accuracy of DFT for ground state properties, it has known deficiencies in correctly reproducing electronic band gaps, d-band positions, and band alignment at interfaces, all of which are necessary to correctly describe the electronic properties of InN nanostructures.
Goal of our visit at the Molecular Foundry, LBL (Berkeley, CA), was to learn and exploit beyond-DFT methodologies (GW based approach) for the simulation of excited state properties of materials and in particular of InN nanostructured systems. Quasi-particle (QP) calculations within the GW approximation [1-3] are known to recover band gaps with an accuracy of ~0.1-0.2 eV. Corrected band structure would provide details on carrier mobilities, charge localization, and affinities for bare or functionalized InN surfaces and NWs.
The long-term goal of this project is to design InN nanoscale architectures (coaxial-nanowires - cNW) able to mimic the processes by which photosynthetic organisms harvest sunlight to convert its energy into more useful forms. Based on a theoretical description of the interfacial and the confinement effects on

charge carriers in nanostructures, inorganic and hybrid (organic/inorganic) nanowires (antenna systems) will be considered, to enable flexibility in the design and to optimize efficiency in energy gain.

In the following I will first describe the GW approach implemented at the Molecular Foundry (LBL, Berkeley) with a detailed description of the required steps to apply GW corrections to DFT calculation, than I will discuss the application of the method to nitrides.

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[2] J. Wu et al *Appl. Phys. Lett.* **80**, 3967 (2002);
[3] T. Matsuoka et al Appl. Phys. Lett. **81**, 1246 (2002).
[4] T. L. Tansley and C. P. Foley, *J. Appl. Phys.* **59**, 3241 (1986).
[5] N. E. Christensen and I. Gorczyca, *Phys. Rev. B* **50**, 4397 (1994); U. Grossner, J. Furthmuller and F. Bechstedt, *Phys. Rev. B* **58**, R1722 (1998); C. Stampfl and C. G. Van de Walle, *Phys. Rev. B* **59**, 5521 (1999), F. Bechstedt et al *Phys. Status Solidi A* **195**, 628 (2003).
[6] J. Furthmuller et al, *Phys. Rev. B* **72**, 205106 (2005).

2. How to set up a GW calculation

The GW implementation that we have learned and applied at the Molecular Foundry is the one outlined in the paper by Hybertsen and Louie [Phys. Rev. B 34, 5390 (1986)] and is based on a plane wave expansion of the solution of the Khon-Sham equation for periodic systems. The calculation proceeds in few steps that are outlined in the followings:

1) First one has to perform a standard DFT calculation and obtain a well-converged density for the system in exam: the Plane Waves cutoff and the Brillouin Zone (BZ) sampling have to be converged. The GW code developed at LBL is interfaced with the DFT code "Paratec" (a standard plane waves DFT code) and it needs to read charge density (CD) and eigenstates in the format produced by this program.

2) Once one has an accurate density (and geometry) one needs to run a series of non self-consistent field (NSCF) calculations to generate different wave functions and eigenvalues that are needed to calculate the self-energy term that enters the expression of the energy corrections to the original Kohn-Sham eigenvalues.

Two NSCF calculations are needed to compute the polarizability (χ) and the dielectric matrix (ε) of the system.

a) The <u>first</u> NSCF will generate a wave function that is called CWFE. In this run the same wave function cutoff of the original DFT run is needed, the BZ sampling could be larger or lower (thus has to be checked but in general it is needed a very good sampling of the BZ) and more importantly a **large number of empty states is needed** (to get a good estimate of the dielectric matrix). The calculation of the dielectric matrix is crucial since it describes the dynamical screening in the solid.

b) The <u>second</u> NSCF is needed to calculate the $\varepsilon(\underline{\mathbf{q}}\rightarrow 0)$ term of the dielectric matrix. This is done by adding in the Paratec input a key word (*gw_shift*) that allows for the calculation of the wave function on a BZ grid that is slightly shifted with respect to the origin (Γ point). This is required because the dielectric matrix is not analytical in $\underline{\mathbf{q}}=0$, but its limit $\underline{\mathbf{q}}\rightarrow 0$ is well defined and it is what counts in the definition of ε. The direction of the small $\underline{\mathbf{q}}$ shift [for example: (0 0 0.01)] in the reciprocal space may influence the final results and a way to defeat this possible source of error is using a large k-point sampling in the NSCF. The wave function generated with this NSCF run has to be called CWFEQ and requires only the occupied states.

At this point one is ready to calculate the polarizability and the dielectric matrix (both CWFE and CWFEQ are used). The polarizability matrix is defined as:

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)=\sum_{n,n'\mathbf{k}}\langle n,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n',\mathbf{k}+\mathbf{q}\rangle\langle n',\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n,\mathbf{k}\rangle\frac{f(\varepsilon_{n',\mathbf{k}+\mathbf{q}})-f(\varepsilon_{n,\mathbf{k}})}{\varepsilon_{n',\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}}$$

χ is a matrix at each **q** point, and is defined as a summation over occupied (n) and unoccupied (n′) states. The convergence over unoccupied states requires a lot of empty states (this is why CWFE has to be obtained with lots of empty states).

Once the polarizability is obtained one can get the dielectric matrix from:

$\varepsilon = 1 + V\chi$

where V is the bare potential; afterwards one calculates the dynamical screened interaction (W) by inverting the dielectric matrix and calculating:

$W = \varepsilon^{-1}V$

this enters the definition of the self-energy operator and thus of the GW correction to the eigenstates of our system [see Phys. Rev. B 34, 5390 (1986)].

In the calculation of ε one needs to specify the *epsilon_cutoff* which defines the dimension of the dielectric matrix to be inverted. In principle one would have to use the entire dielectric matrix, but its inversion is computationally inefficient and time consuming, thus only a submatrix defined by *epsilon_cutoff* is considered. Typical *epsilon_cutoff* values are about 1/10 the cutoff used for the wave functions, of course convergence has to be tested; it is important to have a very well converged dielectric matrix otherwise the GW corrections are not accurate. A way to check if the dielectric matrix is converged is to analyze the value of the reciprocal of the first term of the inverted dielectric matrix ($\varepsilon^{\infty} = 1/\varepsilon_{00}^{-1}$), which represents the macroscopic (experimental) dielectric constant.

Finally a third NSCF is needed to generate the wave functions and the eigenvalues in the point of the BZ where one wants to apply the GW correction. This is done by running a NSCF in a k-point grid that is the same that has been used to compute the polarizability and the dielectric matrix but shifted in the point of the BZ where one wants to compute the correction. It is important that the K and the Q grid have the same spacing, i.e. that they are grids of the same type (nx, ny, nz); it is only the shift that changes. These wave functions are used to compute the self-energy correction calculated at the previous step

3. Nitrides and GW

First-principles calculations should be able to predict a plausible gap value, at least combining the density functional theory (DFT) and the quasiparticle (QP) theory with the exchange-correlation self-energy in GW approximation. The DFT–LDA usually gives reasonable structural parameters and total energies. However, the resulting band structures exhibit the so-called band-gap problem of the semiconductor physics. Taking into account QP corrections, this problem can be solved with an accuracy of about 0.1 eV.

This has been proven for nitrides. The DFT– LDA gap 2.3 (3.9) eV of GaN (AlN) is opened, by a QP correction 1.2 (1.9) eV, to a fundamental gap 3.5 (5.8) eV close to the experimental value 3.5 (6.2) eV [1].

The situation is more complicated for InN. The In4d electrons have to be taken into account to describe correctly the structures of the InN polymorphs [2]. The majority of the DFT–LDA calculations (cf. e.g. Ref. [3]) but also the DFT treatments with an exchange-correlation potential within the generalized gradient approximation [4], however, give rise to negative energy gaps due to an overestimation of the p-d repulsion and, hence, of the shift of the valence-band maximum (VBM) towards higher energies [5]. If one applies GW corrections directly to LDA or GGA eigenstates, the situation is not improved because the starting point of the DFT calculation incorrectly describes the indium energy level ordering and hybridization. One of the approaches that has been proposed in the literature to improve the DFT description of InN consists in the use of self-interaction-corrected (SIC) and relaxation-corrected pseudopotentials [6]. The application of QP corrections on SIC corrected LDA calculations opens the gap from 0.3 (0.4) eV to 0.8 (0.7) eV for wurtzite (zinc blende) which are close to the experimental values.

During the visit to the Molecular Foundry we have first applied GW correction to a simple nitride case (namely AlN) and we have implemented the generation of SIC corrected pseudopotential for InN. With the help of D. Prendergast, working at the Molecular Foundry, we have modified a code that generates pseudopotential and coding a subroutine that add self interaction correction (SIC) during the pseudopotential generation, following the scheme proposed by Pollman et al [PRB 54, 5495 (1996)]. This part required most of the time spent at LBL.

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3.1 : The case of AlN: a “simple” test case

We have performed DFT calculation of AlN in the wurtzite structure by employing Norm Conserving pseudopotentials, an (8 8 8) k-point grid for the BZ sampling (corresponding to 120 K-points) and using the LDA approximation to the exchange and correlation potential.

A convergence test (see figure below), with respect to the energy cutoff for the wave function expansion indicates that a value of about 60-70 Ry has to be used.

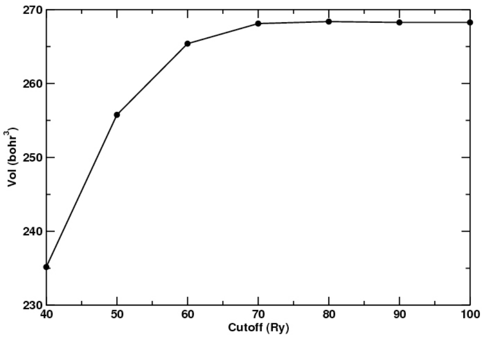

Figure 1 Equilibrium volume of InN (wurtzite structure) as a function of the wave function cutoff (in Rydberg)

The equilibrium lattice vectors at converged cutoff are:

	a (Å)	c (Å)
ECUT 60	3.05065	4.87947
ECUT 70	3.06037	4.89818
ECUT 80	3.06141	4.89971

These values are in good agreement with the experimental values of 3.11 Å and 4.978 Å (from Numerical Data and Function Relationship in Science and Technology, Springer, New York, 1982) and with previous LDA calculations of 3.05 Å and 4.89 Å [PRB 55, 12836 (1997)].

By employing the procedure described in the previous section we have calculated the macroscopic dielectric constant ε^{∞} and the GW corrected energy gap at the Γ point. We tested the convergence of the macroscopic dielectric constant and of the energy gap with respect to the number of empty states employed in the calculation of $\varepsilon(\underline{\mathbf{q}})$ for two different cutoff of the wavefunction (60 and 70 Ry): the results are presented in the following tables (8 **q** points were used to calculate the dielectric matrix and the epsilon_cutoff was 6 Ry).

WF Cutoff 60 Ry			
# Empty bands	ε_{oo}^{-1}	ε^{∞}	ΔE_{Gap} **(eV)**
50	0.22937	4.360	6.514
70	0.22930	4.361	6.537

80	0.22928	4.361	6.544
90	0.22927	4.362	6.546
100	0.22927	4.362	6.546

WF Cutoff 70 Ry			
# Empty bands	ε_{oo}^{-1}	ε^{∞}	ΔE_{Gap} **(eV)**
50	0.22864	4.374	6.410
70	0.22857	4.375	6.433
80	0.22855	4.375	6.441
90	0.22854	4.376	6.442
100	0.22854	4.376	6.442

The values show that already 50 empty states give a small error both on ε^{∞} and on $\Delta E_{Gap.}$ The dielectric constant obtained experimentally is 4.6-4.8 thus our estimated values are less than 5% off. One of the most expensive parts in the GW calculation is the inversion of the dielectric matrix needed to calculate the dynamically screened potential, thus one usually uses a small part of the matrix by using a small cutoff. Effect of the dielectric matrix cutoff (number of empty states fixed at 80) is more pronounced as shown in the following table.

WF Cutoff 70 Ry			
Cutoff	ε_{oo}^{-1}	ε^{∞}	ΔE_{Gap} **(eV)**
4	0.22506	4.443	6.199
6	0.22855	4.375	6.441
8	0.23033	4.342	6.531

The experimental gap value is 6.2 eV (from Numerical Data and Function Relationship in Science and Technology, Springer, New York, 1982).

3.2 The case of InN: a more complicated material.

As mentioned previously, in the case of InN, QP corrections cannot be applied directly to standard DFT calculation because the description of the electronic structure is nor accurate enough. Methods, which allow manipulations of the electron–ion interaction and that lead to gap opening and to a correct energy level ordering in InN have been proven to be a better starting point for QP corrections. For instance, this happens if one employs pseudopotentials in which the self-interaction-corrected (SIC) has been explicitly included [PRB **72**, 205106 (2006)]. Indeed, the SIC approximation gives the correct energetic ordering and occupation of InN bands, thus the quasiparticle effect can be treated in the standard manner within first-order perturbation theory, giving a band gap very close to the experimental value. The SIC correction in not implemented in standard used codes to generate pseudopotentials, thus we spent some time in implementing this correction and following the formalism proposed by Vogel, Rieger, and Pollmann [PRB 54, 5495 (1996)] in the “phipp98” code (a standard code used to generate pseudopotential).

Once the SIC correction has been implemented; we have generated a SIC corrected pseudo for Indium introducing a d-channel in the pseudopotential. This correction gives rise to the following band structure for InN (wurtzite structure) and induces a gap opening of 0.4 eV. This eigenstates have now to be used as starting point for GW calculations.

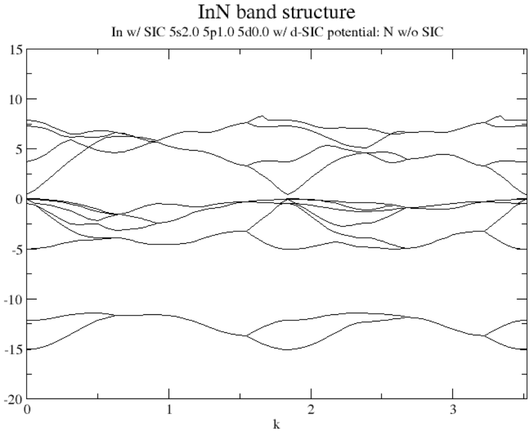

Figure 2 Wurtzite InN band structure obtained by employing a SIC corrected Indium pseudopotential.

4. Future work:

The collaboration with the Molecular Foundry will continue in this year (2008). In particular, given the promising results on the SIC corrected pseudopotential obtained for InN, we will apply GW correction first to bulk InN and than to more complex systems that we have already been relaxed at DFT-LDA level. In the past year (at CNR-IMEM and Politecnico di Torino) we have simulated the ground state properties of InN non-polar surfaces, which are those usually exposed on NWs for successive functionalization. We used ab initio simulations to study functionalization processes at those surfaces: addressing which functional groups (-OH, -COOH, $-NH_2$ and -SH) most likely would attach to them. We investigated the structural properties of small diameter InN nanorods grown in the [0001] direction as observed experimentally. We will apply beyond-DFT methods to the above mentioned InN structures.

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