Cupric oxide as low-cost photovoltaic material : a combined DFT and experimental study

Peng, Yuan

2015

Peng, Y. (2015). Cupric oxide as low-cost photovoltaic material : a combined DFT and experimental study. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62507>

<https://doi.org/10.32657/10356/62507>

NANYANG
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**CUPRIC OXIDE AS LOW-COST PHOTOVOLTAIC
MATERIAL: A COMBINED DFT AND
EXPERIMENTAL STUDY**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

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MATERIAL: A COMBINED DFT AND
EXPERIMENTAL STUDY**

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A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2015

ACKNOWLEDGMENTS

There are many people to thank for their selfish support and help during the past unforgettable journey of my PhD study. In the first place, I want to give my deepest thanks to my supervisor, Associate Professor Wang Junling, for his guide and support during my PhD study. He is a very nice person and is pleasant to deal with. He is very responsible to my research project and provides as much help as he can. His serious scientific attitude and rigorous scholarship deeply infect and inspire me.

I also want to thanks to my co-supervisor Dr. Zheng Jianwei from Institute of High Performance Computing (IHPC), for his invaluable help in my project. His profound knowledge and rich experience in DFT calculations benefit me greatly. His ideas and suggestions help me a lot in solving problems. Thanks to Associate Professor Wu Ping from Singapore University of Technology and Design for his valuable comments and suggestions. I would express my sincere thanks to my mentor Dr. Zhang Zhen, who has taught me how to conduct first-principles DFT calculations and many useful computing tools, for example VASP.

I also want to thanks the School of Materials Science and Engineering for providing resources and funding to this research. In addition, I wish to thank my group members Dr. You Lu and Dr. Zou Xi, for their help to set up the pulsed laser deposition equipment and other generous help during my experiment. I would like to thanks Dr. Wang Baomin and

Dr. Ren Peng for discussion about my thesis project. I also hope to thanks Associate Professor Fang Liang from Soochow University for his generous help.

Finally, I hope to give my warmest thanks to my parents, my husband, my adorable son and other family members for their selfish dedication and understanding. Because of you, my life becomes meaningful and my effort is valuable.

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SUMMARY

Due to low cost and suitable band gap value, cupric oxide (CuO) is of great interest for large-scale photovoltaic application. However, CuO is usually *p*-type and *n*-type CuO is not available. The goal of this study is to understand the behaviour of various dopants and codopants that may affect the electrical conductivity of CuO, and to search for a suitable method to make *n*-type CuO by using first-principles density functional theory calculations followed by experimental studies.

Our DFT calculations identify that copper vacancy can lead to *p*-type CuO, while oxygen vacancy is a deep donor. A systematic study of several potential *p*-type and *n*-type dopants in CuO indicates that Li and Na are shallow acceptors and their formation energies are low in oxygen rich environment. However, it is found that *n*-type conduction is relatively difficult to be achieved by donors, as most donors have deep donor levels in the band gap and/or high formation energies. Hf and Zr have the shallowest donor levels ~ 0.2 eV below the conduction band minimum, but their formation energies are relatively high, indicating low dopant solubility in CuO.

Then, we performed DFT study of donor-acceptor (*n-p*) codoping approach to obtain *n*-type CuO. Our results show that nitrogen codoping can slightly improve the donor levels of Zr and In by forming shallower *n*-type complexes, but the codopant formation energies are so high that it is hard to realize them in experiments. However, it is found that Li codoping with Al and Ga can be achieved easily, because Li codoping can improve

the solubility of Al/Ga in CuO. The corresponding n -type defect complexes have shallower donor levels than those of single Al and Ga donor doping by around 0.1 eV, and their formation energies are reasonably low to act as an efficient codopant. Moreover, Li codoping with both Al and Ga produce an empty impurity band just below the host conduction band minimum, which can reduce the donor ionization energy at high codoping concentrations. Our first-principle calculations suggest that Li codoping can benefit n -type CuO.

To test some of the predictions, experimental studies have been conducted on Li and Zr doped CuO. Our results have shown that Li doped CuO is p -type conductive with the measured resistivity enhanced by more than two orders of magnitude. However, Zr doped CuO is also found to be p -type, because intrinsic copper vacancies is not totally compensated by Zr dopant due to its low solubility in CuO. Overall, our experimental results are consistent with the theoretical predictions.

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1. Y. Peng, J. Zheng, P. Wu, J. Wang "Ab-initio study of donor-acceptor codoping for n-type CuO", *J. Appl. Phys.* **116**, 163704 (2014).
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Chapter I Introduction

This chapter serves as a brief introduction of this thesis. Section 1.1 describes the fundamental of a p - n junction solar cell and the current status of its development. The idea of using cupric oxide (CuO) as an alternative material for large-scale photovoltaic deployment will be discussed. Section 1.2 covers the crystal structure and basic optical and electrical properties of CuO. The detailed review on previous work related to CuO is given in section 1.3. In section 1.4, the objective of this work is described together with the methodologies that will be used. The outline of this thesis is given in section 1.5.

1.1 P-N Junction Solar Cells and Low-cost Alternatives

Currently, the predominant electricity supply in the world is from fossil fuels, which are facing many challenges such as rising prices, growing environmental problems, as well as finite stocks in the earth. Therefore, there are demands to develop alternative energy sources to meet the sustainable development of economics. Renewable energies including solar energy, biomass energy, hydroelectricity and wind power have emerged as potential alternatives to solve the above concerns. Among these new energy sources, solar energy has been growing very rapidly, because it is inexhaustible, available worldwide and clean.

Figure 1.1: Band diagrams of a p - n homojunction solar cell (a) in the dark, and (b) under illumination.

A solar cell is an electrical device which can convert the solar energy into electricity by using the photovoltaic effect. When the photo energy is higher than the value of band gap, the electron in the valence band is excited to the conduction band, generating electron-hole pairs. This process is called photo-generation of free carriers. The photo-generated electron and hole can move freely inside the semiconductor before they recombine with each other. Therefore, a mechanism is needed to separate the charge carriers inside a solar cell. In figure 1.1, the band diagrams of a p - n homojunction solar cell are presented. The Fermi level difference leads to the electron redistribution and band bending around the interface. Because of the internal electrical field, electrons drift into the n -type side while holes drift in the opposite direction. Outside the interface region, carriers continue to diffuse due to the concentration gradient, leading to current flow in the external circuit.

The first efficient solar cell was developed at Bell lab using a silicon p - n junction in 1954. Currently, the efficiency of crystalline silicon based single p - n junction device has

approached its theoretical limit of 33.7% [1], which however is too expensive for large-scale application. Thin film technologies can reduce the amount of light-absorbing materials needed and have better promise of low cost and flexibility as compared with single crystal silicon cells. CdTe [2], CIGS [3] and amorphous silicon [4] are the three main materials used in thin-film solar cells.

However, the solar energy industry is currently facing the serious technical and cost issues, hindering its development. For example, the purification and production processes of crystalline silicon cause pollution to the environment, and the cost per watt is much higher than conventional energy sources, limiting its large-scale production. Cadmium telluride (CdTe) solar cell contains toxic element Cd, while copper Indium Diselenide (CIS) cell uses rare element indium.

For large-scale application, it is necessary to explore other light-absorbing materials that are low-cost, abundant in the earth and environmental friendly. Semiconductor oxides are potential alternatives to the silicon solar cells because they are cheaper to produce, non-toxic and possess high light absorption efficiency. Since the solar spectrum is mainly composed of visible light with wavelength in the range of 380 to 780 nm, only oxides with a band gap smaller than about 3 eV can absorb the visible light. For example, ZnO and TiO₂ with band gap around 3.2 eV are well-known transparent oxides, which can absorb the solar light only in the ultraviolet region of the solar spectrum. It is proposed that the semiconductor should possess an optical band gap of 2 eV or below to better utilize the solar energy.

Figure 1.2: The natural logarithm of the values of material extraction cost and annual electricity potential for 23 semiconductors divided by those for crystal Si as from reference 5. The negative X- and positive Y-values indicates lower cost and higher electricity potential, respectively.

Cyrus Wadia *et al.* have examined the material extraction cost and annual electricity potential for many semiconductors [5], which are compared with the values of silicon crystal solar cells as shown in figure 1.2. Semiconductors in the upper-right quadrant possess less cost and larger electricity potential than Si, and thus can be used as alternative solar cell materials. It is noted that both CuO and Cu₂O are among them, which have small band gaps of 1.35 eV [16] and 2.0 eV [14], corresponding to theoretical solar energy conversion efficiency of 31% [6, 7] and 20% [8], respectively.

Copper oxides are abundant in the earth and non-toxic. Copper oxide thin films and nano materials can be fabricated using various techniques including low-cost chemical process. Compared with Cu_2O , CuO is superior for solar energy harvesting because of its smaller optical band gap. CuO can absorb the whole spectrum of visible light, while Cu_2O can only absorb the part of light with wavelength smaller than 620 nm. Besides, CuO is more stable in air, while Cu_2O can be oxidized into CuO for increased temperatures. In recent years, CuO has received increasing interest due to its promising application for solar energy harvesting.

1.2 Basic Structure and Properties of CuO

1.2.1 Crystal Structure of CuO

CuO has the monoclinic crystal structure with a point group of $2/m$. The unit cell of CuO is shown in figure 1.3. There are eight atoms per primitive unit cell with a space group of $\text{C}2/c$. The four copper atoms are positioned at $(1/4, 1/4, 0)$, $(3/4, 3/4, 0)$, $(1/4, 3/4, 1/2)$, and $(3/4, 1/4, 1/2)$, and the four oxygen atoms occupy positions $(0, u, 1/4)$, $(1/2, 1/2+u, 1/4)$, $(0, -u, 3/4)$, and $(1/2, 1/2-u, 3/4)$. Here, u is the internal parameter of the monoclinic structure, which is equal to 0.4184 as reported in ref. 9. The lattice parameters of CuO unit cell are $a=4.684 \text{ \AA}$, $b=3.423 \text{ \AA}$, $c=5.129 \text{ \AA}$, $\alpha=90^\circ$, $\beta=99.5^\circ$, and $\gamma=90^\circ$. Each copper atom has four nearest neighbour oxygen atoms in a square-like planar configuration. The average Cu-O distance is $1.9475 \text{ \AA}$. The shortest distance between copper atoms is $2.90 \text{ \AA}$, about $0.2 \text{ \AA}$ longer than the sum of two 'Slater-radii' for Cu, indicating that there is no metal-metal bonding in CuO . The building elements of

CuO crystal structure are the oxygen coordination parallelograms, which form chains by sharing edges. There are two types of chains with directions along $[1\ 1\ 0]$ and $[-1\ 1\ 0]$ respectively, which alternate in the $[0\ 0\ 1]$ direction. Each type of chain is stacked in the $[0\ 1\ 0]$ direction with a separation of about $2.7\ \text{\AA}$.

Figure 1.3: The unit cell of CuO (left) and part of the crystal structure of CuO (right). Red balls denote oxygen atoms while melon red balls denote copper atoms.

The equilibrium phase diagram of the Cu-O system at elevated temperatures is shown in figure 1.4, which is divided into three different regions corresponding to three phases of the Cu-O system: CuO, Cu₂O and copper metal. According to the phase diagram, single phase cupric and cuprous oxide films can be achieved by adjusting the substrate temperature and oxygen partial pressure as observed in ref. 10-11. However, for films deposited on substrates with relatively low temperatures, the mixed phases of both Cu/Cu₂O and Cu₂O/CuO have been observed depending on the temperature and oxygen partial pressure [12-14].

Figure 1.4: The copper-oxide phase diagram.

1.2.2 Optical and Electrical Properties of CuO

The electronic structure of cupric oxide has been investigated by many experimental methods, including photoelectron, Auger electron, *etc*, which has demonstrated CuO as a charge-transfer gap insulator in spite of the Cu *d*-O *2p* hybridization [15]. Bulk CuO has an indirect band gap of 1.32 eV at room temperature. The optical absorption edge and tail change largely as the temperature varies between 10 K and 300 K for CuO as shown in figure 1.5, due to the strong coupling of the electronic states with the lattice [16]. CuO powder is black in color, while its thin film is partially transparent in the visible range depending on the thickness. The measured optical band gap of CuO shows a large

variation between 1.3-1.7 eV in the experiment depending on the microstructure and grain sizes [17-19]. For CuO thin films, both in-direct and direct optical band gaps (E_g) are reported in the literature by fitting the absorption coefficient (α) vs $(h\nu - E_g)^2$ (in-direct) or $(h\nu - E_g)^{1/2}$ (direct), leading to different band gap values (see figure 1.6) [18]. The optical band gap also slightly depends on the orientation of CuO thin film. A blue shift in the optical band gap should be expected as the size of CuO particle decreases to several tens of nanometers because of the quantum confinement effect [19]. Annealing of CuO thin film in oxygen or atmosphere can help to increase its light absorbance, when other forms of copper oxide are oxidized into high valence state cupric oxide.

Figure 1.5: Absorbance of single crystalline CuO as a function of temperature [16].

As a semiconductor, the electrical properties of pure CuO are mostly determined by the dominant intrinsic defects, like copper and/or oxygen vacancies. It has been thought that copper vacancies are the dominant point defects in a nonstoichiometric cupric oxide,

due to the volatility of copper [20-22]. Copper vacancies give rise to shallow acceptor levels just above the valence band, which leads to *p*-type behavior [23]. As expected, the *p*-type conductivity will depend on the number of copper vacancies. The reported electrical conductivity of CuO is in the range of 0.01-0.001 S/cm, depending on the methods of preparation. Li element doping can be utilized to increase the hole carrier concentration and decrease the resistivity in CuO [19, 21], since Li substitution at the copper site should act as a *p*-type dopant. On the contrary, *n*-type CuO is difficult to achieve. Both oxygen vacancy and copper interstitial are predicted to be deep donors and thus can not contribute many electrons to the conduction band [23].

Figure 1.6: Absorption spectra (A) and dependence of α^2 (B) and $\alpha^{1/2}$ (C) on photon energy for the randomly oriented (a) and (002)-oriented CuO layers (b) prepared on the transparent conductive glass and (111)-Au/Si substrates [18].

1.3 Previous Work on CuO: Experimental and Theoretical Studies

In the past, copper oxide has been investigated intensively as the basis of several high- T_C superconductors, due to their similar characteristics such as copper-oxygen coordination and magnetic properties [29]. Furthermore, CuO has been used in many other applications such as photothermal device [24], catalysis [25, 26], and gas sensors [27, 28]. In recent years, CuO and Cu₂O have gradually gained attention as promising candidates for large scale solar energy harvesting materials.

FTO/CuO/C₆₀/Al solar cells have been fabricated by spin-coating, where *p*-type CuO acts as the active layer combined with *n*-type C₆₀ to form a heterojunction. However the record efficiency is very low at 1.5×10^{-4} % [30]. High quality CuO films should be critical to improve the efficiency of CuO based solar cell by increasing minority carrier life time and decreasing photocarrier recombination rate. Raksa *et al.* has reported improved performance in ZnO dye sensitized solar cells (DSSCs) when a CuO/ZnO barrier layer is used to control the carrier recombination dynamics in ZnO [31]. Lim *et al.* reported 0.04% efficiency for a CuO/PCBM solar cell [32]. Despite the suitable band gap, the energy conversion efficiency of CuO based solar cells is far below the theoretical limit. In order to reach the full potential of CuO for solar energy harvesting, it is necessary to make a *p-n* junction using both *p*- and *n*-type CuO. However, highly conductive *n*-type CuO has not been achieved so far. Similar problem exists for Cu₂O as well, though the highest reported efficiency for Cu₂O based solar cell is about 2%.

Recently, a few groups have reported *n*-type conduction in CuO [33-35]. Lu *et al.* has

shown that *p*-type Cu₂O can be converted into *n*-type CuO when the oxygen partial was increased during direct current reactive magnetron sputtering with copper target [33]. The measured electron concentration is explained with the oxygen vacancies being present in the sample, which however contradicts with the theoretical prediction of oxygen vacancy as a very deep donor [23]. Figueiredo *et al.* reported *n*-type CuO with the electron concentration around 10^{17} cm^{-3} obtained by annealing metallic copper thin film in air at above 350 °C. However, the mechanism underlying the reported *n*-type behavior is still under debate. Besides, external *n*-type dopant has been tested to modify the electrical properties of CuO. For example, Suda *et al.* have tested Al element doping in CuO, but the sample only showed reduced *p*-type conductivity [21].

The electronic structure of CuO has been studied using density functional theory (DFT) with local spin density approximation (LSDA), which however fails to predict the semiconducting ground state [36-38], because DFT is well known to underestimate the band gap of semiconductors by using the approximate exchange-correlation functionals for electron-electron interactions in real systems. This problem is more serious for transition metal oxides such as CuO, due to strong electron correlation interaction. Although some advanced methods, for example the self-interaction correction (SIC) [39, 40] and the GW approximation [41-43] can provide nearly perfect descriptions of the excited state properties of CuO, they demand heavy computing power, and are still not available for large systems, such as the supercells needed for defect/dopant calculations. Recently, the hybrid functional calculations have also been utilized to resolve the

band-gap problem of standard DFT [47-48], which is very cost-expensive and is hard to be applied to large supercells.

An alternative is the LSDA+U method, which takes into account the on-site repulsion among localized *d-d* electrons by adding the Hubbard term to the energy functionals. It has been proved to be very successful in predicting transitional metal oxides [44-46], including CuO. In the literatures, the electronic structure of CuO has been successfully described by using the LSDA+U method [23, 49]. By using the supercell approach, Wu *et al.* have studied the native point defects in CuO with the LSDA+U method [23]. They concluded that V_{Cu} (copper vacancy) is a shallow acceptor, but V_O (oxygen vacancy), Cu_i (copper interstitial), and Cu_O (copper antisite) are all deep donors, which suggest that CuO is intrinsically a *p*-type semiconductor, and *n*-type conduction in undoped CuO is unlikely. Hu *et al.* have studied various models of CuO surfaces in different crystalline directs including (1 1 1), (-1 1 1), (1 1 0), (0 1 1), (1 0 1), (0 1 0), and (1 0 0) [50]. The results show that CuO (1 1 1) is the most stable facet of CuO. Besides, the antiferromagnetic ordering in CuO has been studied by examining the spin exchange interactions on basis of first-principles DFT electronic structure calculations [51].

It is well known that the electrical properties of semiconductors are often controlled by intrinsic defects and impurities existing in small concentrations, as well as extrinsic dopants. To reach the full potential of CuO for solar energy harvesting, it is necessary to understand the effects of both intrinsic defects and extrinsic dopants on the electrical properties of CuO. In this aspect, first-principles calculations using density functional

theory (DFT) is very useful. It is a fast-developing theoretical method that has been extensively used to obtain comprehensive knowledge of the fundamental processes that control doping, and give directions for experimental investigations [52-56]. A lot of DFT studies have been reported in a wide range of semiconductors such as ZnO [57-59], GaN [60], transparent conducting oxides [61], etc, which examine the dopant solubility in materials and the choice of dopant sources.

The supercell method with periodical conditions is the most common approach to study defects in solids [62]. With the increasing computing power, it is now possible that a large supercell is used to avoid the finite-size effects [63], and to reach high level of accuracy. First-principles DFT calculations can be used to determine a wide range of properties, such as the ground-state structure, electrical and magnetic properties, as well as the thermodynamic equilibrium solubility of defects [59-61], and the kinetic factor such as the migration barrier [64]. The thermodynamic equilibrium concentration of a defect is governed by the formation energy for which a general formalism has been developed based on the total energy calculations [65, 66].

1.4 Objectives of this Work

As a potential low-cost photovoltaic material, it is important to obtain both *p*- and *n*-type CuO through doping so that a *p-n* junction solar cell can be constructed. Though as-grown CuO is usually *p*-type due to the intrinsic copper vacancies, it is difficult to control the carrier concentration. Furthermore, *n*-type CuO can not be obtained using intrinsic defects only. Relevant theoretical studies on the extrinsic doping in CuO are still

missing in the literature, which however could provide important and effective guidance for further experimental investigations. The objectives of this work are (1) to perform DFT calculations to identify potential extrinsic *p*- and *n*-type dopants for CuO; (2) to examine the effect of donor-acceptor (*n-p*) codoping on reducing donor ionization energies in CuO by first-principles DFT calculations; and (3) to test some of the dopants experimentally.

The dopant candidates are carefully selected so that their ionic sizes match with those of host ions, for example, Cu^{2+} . We have systematically examined group IA elements for *p*-type doping, and group IIIA elements and group IVB elements for *n*-type doping. The formation energy of each dopant and the defect level in the band gap are obtained. To examine the *n-p* codoping effect, we have conducted extensive calculations on different combinations of donor and acceptor and calculated the formation energies and transition energy levels for possible *n*-type complexes, which will be compared with the results of single *n*-type dopants. Finally, preliminary experiments are conducted to verify our theoretical predictions.

1.5 Outline of the Thesis

The rest of the thesis is organized as follows:

In Chapter II, I introduce the calculation method that will be used in this work. A brief introduction of first-principles DFT is given, including the LDA and GGA method. Pseudopotential and DFT+U approach are discussed.

Chapter III contains crystal and electronic structures of CuO obtained using the DFT and DFT+U methods which are compared with experimental results. This is to establish the accuracy of the calculations. The theoretical lattice parameters obtained in this chapter will be used for further calculations.

Chapter IV presents the calculated formation energies of point defects in CuO. Our calculations confirm that copper vacancy can lead to good *p*-type CuO, while oxygen vacancy is a deep donor. Li and Na substitutions have been predicted as shallow acceptors with low formation energies, while Zr and Hf substitutions are relatively shallow donors with high formation energies. Other *n*-type dopants including Al, Ga, and Ti are predicted to be deep donors. Our results are consistent with experimental observations and can explain why it is hard to obtain *n*-type CuO.

In Chapter V, I introduce the donor-acceptor (*n-p*) codoping method, which is intended to reduce the donor ionization energy in CuO. The calculated donor levels of *n*-type defect complexes are enhanced compared with those of single *n*-type dopants. It is also shown that N codoping with Zr and In is hard to be realized, while Li codoping with Al and Ga is relatively easy to achieve in experiments. Moreover, Li acceptor codoping with Al and Ga can lower the conduction band minimum of CuO by as much as 0.2 eV at high codoping concentrations, which can help to reduce the donor ionization energies in CuO.

Experimental confirmation of (some of) the theoretical predictions, conclusions and suggestions for future work are covered in Chapter VI and Chapter VII, respectively.

Chapter II First Principles Calculations Based on Density Functional Theory

With the rapid development of large-scale computing capability, DFT has become the dominant method for the quantum mechanical simulation of various systems. In this chapter, a simple introduction of DFT is presented, including Hohenberg-Kohn theorem, Kohn-Sham equations, and exchange-correlation functionals. The DFT+U method for the calculations of transition metal oxides is discussed. Other concepts relevant to this study, such as Bloch's Theorem, k -point sampling, and pseudopotential approximation are also introduced.

2.1 Elementary Quantum Mechanics

The word, *first principles*, or *ab initio*, refers to the calculation of a physical quantity starting directly from established laws of physics, contrary to the classic force field which uses empirical results or fitted parameters. For example, in an *ab initio* approach, the electronic structure is calculated based on Schrödinger's equation using some necessary approximations, instead of fitting some models to match the experimental data. Therefore, first-principle calculations can provide an accurate initial approximation for important questions in physics, chemistry and materials science, which however can not be solved in experiment.

In many-body interacting systems, it has been a challenging problem to solve the static

Schrödinger's equation:

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i \Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \quad (2-1)$$

In this equation, $\hat{H}$ is the Hamiltonian, M and N is the number of nuclei and electrons, respectively. Ψ_i is the wavefunction, corresponding to the eigenvalue E_i . The Hamiltonian $\hat{H}$ is composed of several parts: the kinetic energy of nuclei and electrons (T_N and T_e), and the Coulomb interaction within or between nuclei and electrons ($V_{ee}(r), V_{NN}(R), V_{Ne}(r, R)$):

$$\hat{H} = T_N + T_e + V_{ee}(r) + V_{NN}(R) + V_{Ne}(r, R) \quad (2-2)$$

$$\hat{H} = -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_i^2 - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (2-3)$$

Due to their much larger masses, the movement of nuclei is much slower compared with electrons. Therefore, the electrons can be treated as moving in the potential field produced by fixed nuclei, which is called *Born-Oppenheimer approximation*. In this case, the kinetic energy of nuclei is neglected and the Coulomb energy between nuclei should be a constant. Thus, the Hamiltonian in equation (2-3) is reduces to below for electrons:

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} = T_e + V_{ee} + V_{Ne} \quad (2-4)$$

The solution of the Schrödinger equation with electronic Hamiltonian $\hat{H}_{elec}$ is the electronic wave function of Ψ_{elec} and the electronic energy E_{elec} . The total energy of the system E_{tot} is then the sum of E_{elec} and the constant nuclei repulsion term $V_{NN}(R)$:

$$\hat{H}_{elec} \Psi_{elec} = E_{elec} \Psi_{elec} \quad (2-5)$$

$$E_{tot} = E_{elec} + V_{NN}(R) \text{ where } V_{NN}(R) = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2-6)$$

For a system in the state Ψ , the expectation value of energy is determined by

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{where} \quad \langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^* \hat{H} \Psi d\vec{x} \quad (2-7)$$

In the *variational principle*, it is stated that the energy calculated from a guessed state Ψ should be an upper bound to the true ground state energy E_0 :

$$E_0 \leq E[\Psi] \quad (2-8)$$

To minimize the energy functional $E[\Psi]$ for all allowed N-electrons wave functions will lead to the ground state Ψ_0 and $E[\Psi_0] = E_0$. For a system of N electrons and fixed nuclear potential V_{ext} , the ground state energy can be written as:

$$E_0 = E[N, V_{ext}] \quad (2-9)$$

In the *Hartree-Fock approximation*, the wave function of the system can be approximated by the Slater determinant, an antisymmetrized product of one-electron wave functions. By utilizing the variational principle, one can derive and solve a set of N-coupled equations, yielding the Hartree-Fock wave function and energy of the system. The problem is solved numerically using nonlinear method such as iteration, because there are no known solutions for many-electron systems, namely "*self-consistent field method*".

In the Hartree-Fock method [67], electron exchange is fully accounted for while electron correlation is totally ignored for the electrons with opposite spin, but is taken into account for electrons with parallel spin, which leads to large deviations from experimental results. Density functional theory, which takes into account both electron exchange and correlation energies, albeit approximately, is one of the most common

alternatives to Hartree–Fock calculations.

2.2 Density Functional Theory

Density functional theory (DFT) is a well-known successful approach to solve the Schrodinger equation for many-electron systems. In the 1960s, DFT was established with the development of Hohenberg-Kohn theorems [68] and Kohn-Sham scheme [69], which are the solid foundations to modern DFT. Although remarkable progress has been witnessed, the advantages of DFT started to be taken only when modern supercomputers were affordable years after. Because of their contribution to the development of DFT and computation methods in quantum chemistry, Walter Kohn and John Pople [70, 71] were awarded the Noble Prize in 1998.

2.2.1 The Hohenberg-Kohn Theorems

The electron density is a very important quantity in density functional theory, which gives the probability to find electrons in the space. In Hohenberg-Kohn theorem, it was firstly proven that all the ground-state properties of a system can be uniquely determined by the electron density. Thus, the total energy as well as other physical quantities can be expressed as a unique functional of the electron density as:

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho], \quad (2-10)$$

$$F_{HK}[\rho] = T[\rho] + E_{ee} \quad (2-11)$$

Therefore, the variants of N-particle system are decreased from 3N to 3. $F_{HK}[\rho]$ is the sum of the electron kinetic energy $T[\rho]$ and the electron-electron interaction

energy, $E_{ee}[\rho]$. However, the explicit forms of these functionals ($T[\rho]$ and $E_{ee}[\rho]$) are completely not known, which is the major challenge of DFT.

In the second Hohenberg-Kohn theorem, it is stated that the electron density that minimizes the total energy is the exact ground state density. This assumption is similar as the variational principle:

$$E_0 \leq E[\tilde{\rho}] = E_{Ne}[\tilde{\rho}] + T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \quad (2-12)$$

Therefore, for any trial density $\tilde{\rho}(\vec{r})$ which satisfies the necessary boundary conditions including $\tilde{\rho}(\vec{r}) \geq 0$ and $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$, and which is related to the external potential $V_{ext}(\vec{r})$, the energy obtained from the functional of Eq. (2-12) represents an upper bound to the ground state energy E_0 . The applicability of the variational principle is limited to the ground state. Hence, we cannot easily apply this strategy to the problem of excited states.

2.2.2 The Kohn-Sham Equations

The formalism which was introduced by Kohn and Sham [69] is important for the application of density functional theory in solid state physics and computational chemistry. In *Kohn-Sham scheme*, a fictitious system of non-interacting particles is assumed to generate the same density as any given system of interacting particles. Those non-interacting particles move within an effective Kohn-Sham single-particle potential. The Kohn-Sham method greatly simplifies the calculation of ground state for interacting systems.

As stated in the Hohenberg-Kohn theorem, the ground state energy of a system can be obtained by minimizing the energy functional. The variational problem for the Hohenberg-Kohn density-functional can be written as:

$$\delta[F[\rho] + \int v_{ext}(r)\rho(r)dr - \mu(\int \rho(r)dr - N)] = 0 \quad (2-13)$$

where μ is a Lagrange multiplier to constrain the number of electrons to be N . The universal functional of $F[\rho]$ can be written as a sum of the kinetic energy $T[\rho]$, the classical Coulomb interaction $J[\rho]$ (also called Hartree energy) and the non-classical portion $E_{ncl}[\rho]$:

$$F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] \quad (2-14)$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} dr_1 dr_2 \quad (2-15)$$

Of these, only $J[\rho]$ is known. It comes to the problem to find the expressions for $T[\rho]$ and $E_{ncl}[\rho]$. To solve this problem, Kohn and Sham proposed a non-interacting system of electrons, whose kinetic energy $T_s[\rho]$ can be determined exactly. The ground state wave function Ψ_{KS} for a non-interacting system can be given exactly by a determinant of single-particle orbitals $\Psi_i(r_i)$,

$$\Psi_{KS} = \frac{1}{\sqrt{N!}} \det[\Psi_1(r_1)\Psi_2(r_2)\dots\Psi_N(r_N)] \quad (2-16)$$

The universal functional $F[\rho]$ could be divided into three parts:

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (2-17)$$

where $E_{xc}[\rho]$ is the exchange-correlation energy:

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + E_{ncl}[\rho] \quad (2-18)$$

which contains the non-classic part of kinetic energies and also the non-classic contribution to the electron-electron interaction.

Equation (2-13) can be rewritten as:

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho(r)} + V_{KS}(r) \quad (2-19)$$

in which the Kohn-Sham potential $V_{KS}(r)$ is given by:

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + \int \frac{\rho(r')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}(\vec{r}) \quad (2-20)$$

and the exchange-correlation potential $V_{xc}(\vec{r})$ given by:

$$V_{xc}(\vec{r}) = \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \quad (2-21)$$

To obtain the ground state density, it is practically to solve the N one-electron Schrödinger equations for a non-interacting system of particles moving in an effective external potential $V_{KS}(r)$, which is called the Kohn-Sham equations:

$$\left[-\frac{1}{2} \nabla^2 + V_{KS}(\vec{r}) \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (2-22)$$

where is ε_i the Lagrange multipliers of the orthonormality of the N single-particle states. The density is constructed from,

$$\rho(r) = \sum_i^N |\psi_i(r)|^2 \quad (2-23)$$

The non-interaction kinetic energy is therefore given by,

$$T_s[\rho] = -\frac{1}{2} \sum_i^N \int \psi_i^*(r) \nabla^2 \psi_i(r) dr \quad (2-24)$$

The total energy of the system containing N non-interacting particles can be summed over one-electron eigenvalues ε_i . Since $V_{KS}(\vec{r})$ is also a functional of the density, the

Kohn-Sham equations can only be solved iteratively or self consistently. Because of the convex nature of the density-functional, it is of course to converge to the ground-state minimum.

It is noted that those orbitals $\Psi_i(r_i)$ have no physical significance. However, the computational effort required to solve the Schrödinger equation for the non-interacting orbitals $\Psi_i(r_i)$ scales as the cube of the system-size N , due to the cost of diagonalizing the Hamiltonian or orthogonalizing the orbitals.

It is very important to note that if we knew the exact form of the exchange-correlation energy $E_{xc}[\rho]$ for interacting electron system, the Kohn-Sham method would lead to the exact energy. The intention of the Kohn-Sham method is to make the unknown contribution of exchange-correlation energy to the total energy as small as possible. However, the exchange-correlation energy contribution is in most cases not a negligible term and usually comparable to the binding energy. Therefore, an accurate description of the exchange-correlation energy is crucial for the prediction of ground state properties of interacting systems.

2.2.3 Exchange-Correlation Functional

To practice Kohn-Sham scheme, it is crucial to know the accurate description of exchange and correlation interactions, which however is difficult. But simple approximations for the exchange-correlation energy can also work extremely well in most cases. The *local density approximation* (LDA) is the fundamental form of all the other approximate exchange-correlation functionals, which was given by Kohn and Sham

in 1965 [69]. The main idea of LDA is that the real inhomogeneous electronic systems can often be regarded as locally homogeneous and the exchange-correlation functional can be approximated by the corresponding energy of a homogeneous electron gas.

In the LDA, the exchange-correlation energy can be written as following:

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r} \quad (2-25)$$

Here, $\varepsilon_{xc}(\rho(\vec{r}))$ is the exchange-correlation energy per electron for a uniform electron gas density $\rho(\vec{r})$. The quantity $\varepsilon_{xc}(\rho(\vec{r}))$ can be divided into exchange and correlation contributions,

$$\varepsilon_{xc}(\rho(\vec{r})) = \varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r})) \quad (2-26)$$

The exchange part, ε_x , was given by Bloch and Dirac in the 1920's in a functional of the uniform electron gas density,

$$\varepsilon_x = -\frac{3}{4} \left(\frac{3\rho(\vec{r})}{\pi} \right) \quad (2-27)$$

However, we do not know the explicit expression for the correlation energy, ε_c . Several groups have reported their solutions to the correlation energy expression, for example, the numerical quantum Monte-Carlo simulations of the homogeneous electron gas by Ceperly-Alder in 1980 [72], which was further parameterized by several groups, including Perdew-Zunger [73], Vosko-Wilk-Nusair [74], and Perdew-Wang [75], etc. Although it seems to be a crude approximation for real systems of rapidly varying electron density, the success of LDA at predicting physical properties in real systems, especially the ground state properties, is surprising. However, LDA often overestimates the binding energy of molecules, which is not sufficient for applications in chemistry.

General semilocal approximation to the exchange-correlation energy is the *generalized gradient approximation* (GGA), as a functional of the electron density and its gradient (the first derivative of the electron density), since the electron density of real systems is generally non-uniform. Thus, we write the exchange-correlation energy in terms of an analytic function known as the enhancement factor, $F_c[\rho(r), \nabla\rho(r)]$, which directly modifies the LDA,

$$E_{xc}^{GGA}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) F_c[\rho(r), \nabla\rho(r)] d\vec{r} \quad (2-28)$$

The gradient of the density is usually determined numerically. Much thoughtful work has been done to develop gradient corrected functional forms, leading to important progress in GGA, including PW86 (Perdew and Wang 1986) [76], PBE (Perdew, Burke, and Ernzerhof) [77], and PW91 (Perdew and Wang 1991) [75], etc, which are tailored for special classes of problems. Further development after the GGA is the meta-GGA functionals by including the second derivative of the electron density.

In conclusion, both LDA and GGA are important approximations for the exchange-correlation functionals within the DFT scheme. The well-known problem of DFT is that it often underestimates the energy band gap of semiconductors. DFT can also fail in predicting strong correlated systems, such heavy fermions and high-temperature superconductor, whose properties are dominated by electron-electron interactions.

2.3 The LSDA+U Approach

In spite of the great success of DFT in describing the ground state properties of most materials, it also has drawbacks, such as the well-known band gap underestimation

problem. The problems are most severe for strongly correlated systems, in which the electrons tend to be localized and strongly interacting with each other, for example, transition metal oxides and rare-earth elements and compounds with partially filled d or f shells. The failure traces back to the use of uniform electron gas to represent exchange, or more importantly to not adequately treating the many-body electronic correlations.

Although some advanced methods such as the self-interaction correction (SIC) [39] and the GW approximation [41] have been developed, they demand heavy computing power. On the other hand, the LSDA+U method was proposed by Anisimov *et al.* [44]. In the LSDA+U method, delocalized s , p electrons were still described by normal DFT method, while the strong intra-atomic interaction for localized d or f electrons is described by adding a Hubbard term to the total energy functionals [45, 46].

In this study, we adopted the simplified (rotationally invariant) form to the LSDA+U, which was introduced by Dudarev *et al.* [78]. The model Hamiltonian to describe localized electrons takes the form of,

$$H = \frac{U}{2} \sum_{m,m',\sigma} \hat{n}_{m,\sigma} \hat{n}_{m',-\sigma} + \frac{U-J}{2} \sum_{m \neq m',\sigma} \hat{n}_{m,\sigma} \hat{n}_{m',\sigma} \quad (2-29)$$

where $\hat{n}_{m,\sigma}$ is the number operator for magnetic quantum number m and spin σ ; U and J denote the effective on site Coulomb- and exchange- parameters. U is the cost of Coulomb energy when two d electrons are placed at the same site,

$$U = E(d^{N+1}) + E(d^{N-1}) - 2E(d^N) \quad (2-30)$$

Then the total energy using the LSDA+U method is expressed as,

$$E^{LSDA+U} = E^{LSDA} + \frac{U-J}{2} \sum_{m,\sigma} \left(\hat{n}_{m,\sigma} - \hat{n}_{m,\sigma}^2 \right) \quad (2-31)$$

To write the above the equation in a form which is invariant with respect to a unitary transformation of orbitals, the number operator $\hat{n}_{m,\sigma}$ is replaced by the on-site density matrix $P_{m,m}^\sigma$ of the d electrons as follows,

$$E^{LSDA+U} = E^{LSDA} + \frac{U-J}{2} \sum_{\sigma} Tr \left[P^\sigma - P^\sigma P^\sigma \right] \quad (2-32)$$

This density matrix is diagonal in the m, m' representation and its eigenvalues equal $\hat{n}_{m,\sigma}$.

The effective on-site Coulomb interaction parameter U is not equal to the Columbic energy between localized d or f electrons whose value is however much bigger. When the strength of U is comparable with the valence bandwidth (W), addition or removal of electrons to the d or f orbital could give rise to large fluctuations of the energy of the system. In this case, the LSDA+ U method should be adopted instead of a mean field approach. The LSDA+ U method has proven to be successful in applications to strongly correlated systems where LSDA fails to describe the electronic and magnetic properties.

2.4 Bloch's Theorem and Plane Wave Basis Sets

Because the ions in a pure crystal are assumed to be at rest in their equilibrium positions, the electrons can be considered to move in a static potential. Because of the periodicity of the crystal structure, the potential is also periodic, which must satisfy:

$$V_{ext}(r) = V_{ext}(r + L) \quad (2-33)$$

where L is the Bravais lattice vector. The periodically-repeating potential is the requirement for the use of Bloch's theorem, which states that the wavefunction for a

particle in a periodically-repeating environment, most commonly an electron in a crystal, can be expressed as the product of two parts: the lattice periodic part and the wavelike part,

$$\psi_{jk}(r) = u_{jk}(r) \exp(ik \cdot r) \quad (2-34)$$

where k is called the crystal wave vector, and u is a periodic function which should have the same periodicity as the crystal. And we can get,

$$u_{jk}(L + r) = u_{jk}(r) \quad (2-35)$$

$$\psi_{jk}(r + L) = \psi_{jk}(r) \exp(ik \cdot L) \quad (2-36)$$

Therefore, by using the Bloch's theorem, one only needs to calculate a finite number of electronic wavefunctions within the unit cell of the Bravais lattice.

On the other hand, the wave vector k can always be confined to the first Brillouin zone of the reciprocal lattice. This is because k in the first Brillouin zone and k' out of the first Brillouin zone satisfy,

$$k' = k + G \quad (2-37)$$

where G is vector in the reciprocal lattice defined by,

$$G \cdot L = 2\pi n \text{ (} n \text{ is an integer)} \quad (2-38)$$

It is possible to use a small set of special k points in the first Brillouin zone, because the electronic wavefunctions and other properties at k points that are very close together will be almost identical. Generally, a dense set of k points can ensure more accurate calculations with sacrifice of the computing cost. A test of the convergence of total energy as increased k -point size is usually necessary. A good k -point sampling method is

critical to minimize the size of k points needed. The Monkhorst-Pack scheme is most suitable for total energy calculations in both metals and semiconductors, while the former usually require more k points to reach enough accuracy. By considering the symmetry and point group, the size of necessary k points can be further reduced.

The lattice periodic function can be expanded in terms of a linear combination of plane wave basis set,

$$u_j(r) = \sum_G c_{j,G} \exp(iG \cdot r) \quad (2-39)$$

where G is the reciprocal lattice vector, and $c_{j,G}$ is the plane wave coefficients. Therefore, the electron wave function can be written as a sum of plane waves,

$$\psi_{jk}(r) = \sum_G c_{j,k+G} \exp[i(k+G) \cdot r] \quad (2-40)$$

The Bloch wave at each k point can be expressed in sum of a discrete plane wave basis set, which is infinite in principle. Fortunately, the plane wave coefficient $c_{j,k+G}$ is inversely proportional to the kinetic energy term $(\hbar^2 / 2m)|k+G|^2$. Therefore, the plane waves with a lower kinetic energy term are more important than those with a high kinetic energy term. Hence, it is reasonable to truncate the plane wave basis set to a finite number by using a cutoff energy E_{cut} ,

$$\frac{\hbar^2}{2m}|k+G|^2 \leq E_{\text{cut}} \quad (2-41)$$

It is noted that the introduction of plane wave energy cutoff can lead to an error in the total energy calculation, which however can be minimized by increasing the cutoff energy. Since the selection of a higher cutoff energy leads to increased computing costs, it is often necessary to perform a total energy calculation to optimize the cutoff energy

first. Furthermore, the core electron wavefunctions require a large number of plane waves, which can be solved by using the pseudopotential approximations.

2.5 The Pseudopotential Approximation

There are two types of electrons in every solid: core electrons and valence electrons. The core electrons are localized in the inner shells of the atoms, surrounding the nucleus, while the valence electrons are distributed in the outer shells of the atoms, participating in the binding between atoms. Therefore, the chemical and transport properties of materials are mostly determined by valence electrons. However, an extremely large plane wave basis set is needed in an all-electron calculation to accurately treat the core-electron wave functions which oscillate rapidly with many nodes. In *pseudopotential approximations*, the core electrons are frozen to the nucleus as a whole to act on valence electrons. The pseudo wavefunctions vary smoothly which have no radial nodes in the core region. By doing so, the number of plane waves needed to expand the electron wavefunctions is largely reduced.

In figure 2.1, an all-electron wavefunction and a pseudo wavefunction are presented. As we can see, the all-electron wavefunction oscillates rapidly in the region occupied by the core electrons due to the strong Coulomb potential. The pseudo and all-electron wavefunctions are identical if $r > r_c$ (core radius),

$$\psi^{AE}(r) = \psi^{PP}(r) \quad (2-42)$$

Figure 2.1: Schematic diagram of the comparison between all-electron and pseudo-potentials and wavefunctions.

There are two types of widely used pseudopotentials. One is the *norm-conserving pseudopotential* (NCPP), which was introduced by Hamann, Schluter, Chiang in 1979 [79]. For a given atomic configuration, the charge density for the NCPP wavefunction must accurately reproduce the valence charge density in the core region. NCPPs are transferrable as their construction ensures that they reproduce the logarithmic derivatives, i.e., the scattering properties of the true potential in a wide range of energies. NCPPs are traditionally split into a local part and a non-local part:

$$V^{PS} = V_{loc} + V_{SL} = V_{loc} + \sum_{l=0}^{l_{\max}} V_l |l \gg l| \quad (2-43)$$

where V_{loc} is the local part, which is long-range and behaves like the electrostatic field generated by the total core and nucleus charges. While V_{SL} is the non-local part, which depends on the short-range potential per angular momentum and is very costly to compute. NCPPs are still difficult to use and require a large plane-wave basis set for

first-row elements and transitional metals. *Ultrasoft* (Vanderbilt) *pseudopotentials* (USPP) are devised to overcome such a problem [80]. USPPs allow the use of much smaller plane-wave basis set in most cases, but the success of the method is partly hampered by the difficulty in the generation of the pseudopotentials. It is also reported that the USPPs can fail in spin-polarized calculations for materials with a large magnetic moment.

Bloch proposed a method to combine the ideas of the pseudopotential and linearized augmented plane wave (LAPW) methods in 1994, which is called the *projector augmented-wave method* (PAW) [81]. The PAW [82] procedure can be used to reconstruct all-electron orbitals from pseudo-orbitals. Generally the PAW potentials are more accurate than the USPPs, because the radial cutoffs used for PAW potential are smaller than the radii used for the USPP and the necessary energy cutoffs and basis sets are also somewhat larger.

Pseudopotential approximation is important for DFT calculations to become an efficient and competing tool in modern quantum mechanical simulations. By using pseudopotential approximation, only valence electron wavefunctions need to be calculated accurately. Moreover, by freezing the core electrons, the interaction between core electrons and nucleus is neglected. Therefore, the total energy generated during pseudopotential calculations is no longer meaningful and only the difference in energy between different electron and ionic configurations is useful.

2.6 Summary

With the *Born-Oppenheimer approximation*, the nuclei are frozen and the problem is to solve many-body electron interactions. When the number of electrons is large, it seems unpractical to give the exact solutions for the Schrödinger's equation. The Hohenberg-Kohn theorem proves that all the ground state properties can be expressed in terms of the electron density. Shortly, the Kohn-Sham scheme which used a system of non-interaction particles moving within an effective potential to solve the problems of interacting particles was proposed. Because the exact expression for the exchange and correlation potential is not known, approximations includes LDA and GGA have been made, which can work extremely well in most cases. Beyond DFT, the LSDA+U method is useful for the electronic structure calculations of transition metal oxides.

Since the chemical and transport properties of materials are mainly determined by the valence electrons, a smooth and non-singular *pseudopotential* is adopted to reduce the computing cost. In a periodical system, the plane-wave basis set is utilized to represent electron wavefunctions. However, those plane waves with larger kinetic energies are less important; therefore, a cutoff energy is utilized to reduce the number of plane-wave basis set. In a periodic potential, the number of k -points in reciprocal space can be reduced to a few points in the first Brillouin zone by symmetry operations and Bloch's theorem.

Chapter III Properties of Pure CuO by LSDA+U Calculations

3.1 Introduction

Cupric Oxide (CuO), a copper oxide semiconductor with a narrow indirect band gap of 1.3 eV at room temperature [16], has been of great interest for applications such as pigment in ceramics, cathode material for wet cell batteries, and a base material for cuprate high-temperature superconductors. Recently, CuO has attracted much attention as a cheap alternative for Si regarding to its application in solar energy harvesting [5]. But the development is hampered by the lack of fundamental knowledge about CuO. Theoretical studies, especially DFT calculations, are useful tools to study the crystal and electronic structures of CuO, as well as the effect of doping on the electrical conductivity in CuO.

However, it is known that DFT calculations tend to underestimate the band gap, and the problem is more serious for transition metal oxides due to the strong repulsion among localized 3d electrons [38]. The exchange-correlation energy between localized Cu 3d electrons contributes significantly to the total energy of the system, which however can not be described very accurately with the approximated density functionals. Some advanced methods which are often utilized for calculations of excited state properties, such as the self-interaction correction (SIC) [39] and the GW approximation [41] suffer

from the heavy demand on computing power. An alternative is the DFT +U method, which solves the problem by adding a Hubbard U term to the total energy functional [44]. Here, we compare the results of DFT and DFT+U calculations, and demonstrate the validity of LSDA+U in calculating the crystal and electronic structures of CuO. We also study the dependence of band gap on the Hubbard U parameter and propose a suitable U value for subsequent investigations.

3.2 Computational Method

The structure relaxation and total energy calculations of CuO are performed using the VASP code [83, 84], where the ground state structure is determined by minimizing the total energy for all atomic configurations. The calculations are performed using density functional theory (DFT) within both local spin density approximation (LSDA) and generalized gradient approximation (GGA). An antiferromagnetic spin ordering is assumed for CuO [85-87]. The Ceperly-Alder (CA) exchange-correlation functional is employed for the LSDA calculation while Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is employed for the GGA calculation. The PAW pseudopotential [81] is adopted, where Cu $3d^{10} 4s^1$ and O $2s^2 2p^4$ orbitals are treated as the valence orbitals.

The unit cell structure used for the calculation is shown in Figure 3.1, which contains four formulas of CuO. The structure optimization is performed by fixing the C2/c symmetry for monoclinic structure. A specific parameter is used to control the degree of freedom for lattice relaxation such as the unit cell volume and shape. Atomic relaxation

is done with a quasi-Newton (variable metric) algorithm where the forces and the stress tensor are used to find the equilibrium positions. The self-consistent energy convergence criterion per atom is 0.1 meV and the Hellman-Feynman forces are converged to less than 10 meV/Å.

Figure 3.1: Unit cell structure of monoclinic CuO used for the calculations.

3.3 Results and Discussion

3.3.1 Cutoff Energy and *K*-points Optimization

The choice of cutoff energy is very important for total energy calculations, which determines the number of plane waves for electron wavefunction expansion. Fortunately, as the kinetic energies of plane waves increase beyond some cutoff energy, the total energy difference introduced by using a larger plane-wave basis set is often negligible. For calculations of unit cell with more than one species of atoms, it is often necessary to conduct a total energy convergence test on the cutoff energy before any structure optimization. In the convergence test, all atoms are fixed at initial positions (static

calculation). The difference in the total energy per unit cell is less than 10 meV when the cutoff energy is increased beyond 600 eV. Therefore, it is safe to set the cutoff energy at 600 eV for subsequent calculations.

Figure 3.2: Convergence test results on the cutoff energy for CuO using GGA.

For the integration in the first Brillouin zone of the unit cell, a denser k -point mesh is usually needed. A finite number of k points generated using the Monkhost-Pack method are used. Convergence tests on the size of k points are also necessary to ensure the validity of the calculations. As shown in Figure 3.3, the total energy fluctuates rapidly for small k -point meshes, however it converges fast as the k -point mesh is larger than $8 \times 8 \times 8$, which generated 128 independent k points. The difference in the total energy is smaller than 0.3 meV when using a larger k mesh. Therefore, a $8 \times 8 \times 8$ Monkhost-Pack k -point mesh is used for the subsequent calculations.

Figure 3.3: Convergence test results on the k -point mesh size for Brillouin zone integrals of the unit cell using GGA.

3.3.2 Crystal and Electronic Structures of CuO by LSDA and GGA Calculations

To obtain the ground state crystal structure, lattice relaxation has been performed with the volume of the unit cell fixed at a set of 20 different values and with the shape of the unit cell relaxed. The calculated total energies E of the relaxed cells are plotted in Figure 3.4 as the functional of the volume V for both LSDA and GGA methods.

By fitting our data to the Brich-Murnaghan equation of states (EOS), one can obtain the ground state energy and volume:

$$E(V) = E_0 - \frac{B_0 V_0}{B' - 1} + \frac{B_0 V_0}{B'} \left[\frac{(V_0/V)^{B'}}{B' - 1} + 1 \right] \quad (3-1)$$

where E_0 and V_0 are the ground state energy and equilibrium volume of per CuO unit cell, B_0 denotes the bulk modulus at zero pressure. The high degree of convergence of the equilibrium energy E_0 is reflected in the smooth character of the “ E - V ” curves in Figure 3.4. The root-mean-square (rms) error of the fit on total energy is about 1 meV. Generally, the EOS fitting is a reliable method, which is widely used in DFT to find out the ground

state crystal structure parameters.

Figure 3.4: EOS fitting of the total energy of CuO unit cell within (a) LSDA and (b) GGA.

The equilibrium volume obtained using LSDA is $82.81 \times 10^{-30} \text{ m}^3$, and it is $90.49 \times 10^{-30} \text{ m}^3$ when GGA is used. As compared with the experimental value of $79.94 \times 10^{-30} \text{ m}^3$, it is overestimated by about 4% and 13.2% for LSDA and GGA, respectively. The results are quite strange, because it is known that GGA usually overestimate lattice constants or volume, while the LSDA usually underestimates them. We also calculated the lattice

parameters at the equilibrium volume. Both LSDA and GGA predict the lattice constants with as large as 19-23% discrepancy with the experiment values (Table 3.1). Therefore, it seems that DFT has difficulty in obtaining the structure parameters accurately.

Table 3.1: Calculated lattice parameters for CuO. The values in the parenthesis are the difference between theoretical and experimental values [9, 16-17].

	a (Å)	b (Å)	c (Å)	β	u	volume (Å ³)
Experiment	4.65	3.41	5.11	99.48	-0.58	79.94
GGA	4.17 (-10.3%)	4.19 (+23%)	5.17 (-1.2%)	90.04 (-9.5%)	-0.5 (-14.4%)	90.49 (+13.2%)
LDA	4.05 (-13%)	4.06 (+19%)	5.06 (-1%)	90.02 (-9.5%)	-0.5 (-14.4%)	82.81 (+3.6%)
LSDA+U ($U_{\text{eff}}=7.5$)	4.56 (-1.9%)	3.27 (-4.2%)	4.96 (-2.96%)	100.2 (+0.7%)	-0.59 (+1.5%)	72.74 (-9%)

The density of states (DOS) obtained are shown in Figure 3.5, which are calculated based on the theoretical lattice constants of CuO unit cell by LSDA and GGA, respectively. The dashed lines in the figures are Fermi levels. Since the Fermi levels in both figures cross the bands and there is no energy gap observed, the calculated electronic structures by both LSDA and GGA indicate that CuO is a metal. However, CuO is a well-known semiconductor with a narrow band gap of ~ 1.32 eV. DFT tends to underestimate the band gap due to the approximation in electron exchange-correlation interaction. The problem is more serious for localized electrons like Cu 3d electrons, where the electron exchange-correlation energy can cause large difference on the total energy.

Figure 3.5: Total DOS of CuO unit cell obtained using (a) LSDA and (b) GGA. Fermi levels run across bands indicating metallic behaviour, contradicting experimental observation.

3.3.3 Crystal and Electronic Structures of CuO by the LSDA+U Method

As we can see above, the theoretical lattice constants and band gap values obtained using both LSDA and GGA differ largely from the experiment ones. Since DFT calculations often fail for strong correlated systems such as transition metal oxides with partially filled d shells, an alternative LSDA+U method is adopted which was proposed by Anisimov *et al.*. In this thesis, we take the simplified approach to the LSDA+U,

introduced by Dudarev *et al.*, where the $U_{\text{eff}} = U - J$ is used instead of separated U and J . Below, we show the calculated crystal and electronic structures by using LSDA+U ($U_{\text{eff}} = 7.5$ eV).

The calculated E - V curve using the LSDA+U method is plotted and fitted to the EOS equation as shown in Figure 3.6. The crystal structure and atom positions are relaxed with the volume fixed for each data point. The equilibrium volume is $72.74 \times 10^{-30} \text{ m}^3$, which is underestimated by 9% as compared with the experiment value of $79.94 \times 10^{-30} \text{ m}^3$ [9]. The calculated lattice parameters at the equilibrium volume are displayed in Table 3.1, with $a=4.56 \text{ \AA}$, $b=3.27 \text{ \AA}$, $c=4.96 \text{ \AA}$, $\beta=100.2$, and $u=0.593$. As we can see, the LSDA+U method predicted lattice constants are only about 1.9%-4.2% smaller than the experimental values [9]. Therefore, by using LSDA+U, the lattice structure of CuO unit cell can be calculated more accurately than pure DFT calculations. Our results also show good agreement with other theoretical predictions [23].

Figure 3.6: EOS fitting of the total energy of CuO unit cell using LSDA+U ($U_{\text{eff}} = 7.5$ eV) method.

Based on the calculated lattice parameters, the band structure of CuO obtained using the LSDA+U ($U_{\text{eff}}=7.5$ eV) is shown in Figure 3.7. The valence band maximum is at the gamma point in the first Brillouin Zone, while the conduction band minimum locates at the D point. Therefore, the computed indirect band gap of CuO is 1.3 eV which agrees well with the experimental value [16]. The notations of the high-symmetry points of the first Brillouin zone are followed from reference [125].

Figure 3.7: Electronic band structure of CuO calculated using LSDA+U ($U_{\text{eff}}=7.5$ eV) method. The indirect band gap is 1.3 eV, which agrees well with the experimental value.

The total and partial density of states (DOS) calculated using LSDA+ U ($U_{\text{eff}}=7.5$ eV) are shown in Figure 3.8. From the partial DOS, the lowest energy band at -18 eV belongs to the oxygen 2s levels. The width of the valence band is about 8.5 eV, which mainly consists of Cu 3d and O 2p levels. The sharp peak at -5 eV in the middle of the valence band comes from the Cu 3d levels. The top of valence band is formed from both oxygen 2p levels and Cu 3d levels. The bottom of the conduction band is dominated by Cu 3d levels, which are quite localized. Therefore, by taking into account the strong correlation

effect by using LSDA+U, the highly localized Cu 3d levels in the middle of valence band are recovered and the hybridization between Cu 3d and O 2p levels is reduced.

Figure 3.8: Total and partial DOS of CuO calculated using LSDA+U ($U_{\text{eff}}=7.5$ eV).

3.3.4 Dependence of Calculated Band Gap on the U Values

The LSDA+U calculation by using $U_{\text{eff}}=7.5$ eV can better describe the electronic structure of CuO than pure DFT calculations, due to the strong correlated interaction between Cu 3d electrons. However, the U parameter depends on particular atoms and materials. Generally, atoms with more partial filled 3d or 4f electrons need a larger U to take into account localized electron correlation effect. Therefore, we study the effect of U values on the electronic band gap of CuO as shown in Figure 3.9. The calculated band gap increases almost linearly with the effective U values. When $U_{\text{eff}}=7.5$ eV, the theoretical band gap agrees to the measured one and the magnetic moment saturates at about $0.63 \mu_B$. We therefore conclude that this value for the effective U is the best for the subsequent calculations of CuO.

Figure 3.9: Dependence of calculated electronic energy gap on the value of U_{eff} with LSDA+U.

3.4 Summary

The equilibrium lattice constants and density of states of bulk CuO have been calculated using DFT. The failure of both LSDA and GGA to describe the ground state properties of CuO is observed, and hence calculations based on LSDA+U method are conducted to solve the problem. By adding a $U_{\text{eff}} = 7.5$ eV to the total energy expression in the Dudarev's model, both theoretical lattice constants and the calculated band gap value agree well with the experiment ones. The calculated band gap also shows dependence on the U_{eff} parameter. The results in this chapter identified the problems of DFT as well as alternative methods for the accurate calculations of CuO, which are necessary for further studies on defects and doping in the following chapters.

Chapter IV Point Defects and Dopants in CuO

Intrinsic defects and extrinsic dopants are important for the electrical properties in CuO. It is of great interest to study the formation of point defects and dopants in CuO using first-principle DFT calculations, which can direct further experimental investigations. The results in this chapter demonstrate that intrinsic copper vacancies lead to the *p*-type conducting behavior in as-prepared CuO. On the other hand, to control the CuO electrical properties, several possible single dopants (*n*-type and *p*-type) have been studied. From the analysis on dopant solubility and ionization level, we proposed the best *p*-type and *n*-type dopants, and also explain why it is difficult to obtain *n*-type CuO.

4.1 Introduction

The theoretical energy conversion efficiency of a CuO based solar cell is 31% [6, 7], comparable with that of crystalline Si solar cell, whose large-scale application in household and industry is hampered by the high cost of crystalline Si. The cost of CuO is however much cheaper. It is expect that even a low efficiency of 5% for CuO solar cell with several micrometers in thickness can reach better performance-price ratio than crystalline Si solar cell. However, it has been very challenging to fabricate highly conductive *n*-type CuO, which limits the development of CuO based photovoltaic devices.

To facilitate the development of CuO for solar energy harvesting, it is important to

understand the fundamental defect physics in this material. Experimentally, it has long been observed that CuO shows *p*-type conduction, which should be related to the native defects such as Cu vacancy due to high evaporation rate of Cu during fabrication [20-23]. The intrinsic *p*-type defects can be a great obstacle for the development of *n*-type CuO, since Cu vacancies act as electron compensating centres. Furthermore, it is difficult to control the concentration of intrinsic defects precisely during experiments. Most as-prepared CuO samples have high electrical resistivity above 1000 $\Omega \cdot \text{cm}$. For solar cell application, the optimized resistivity should be around 1-10 $\Omega \cdot \text{cm}$ to reduce the energy loss due to joule heating inside the solar cell devices.

Therefore, we first investigate the formation of intrinsic defects in CuO by using total energy calculations and supercell method. The dominant intrinsic defect types under different thermo-chemistry conditions (oxygen rich and oxygen poor) are identified. To control the electrical properties of CuO, we carefully select a series of potential *p*-type and *n*-type dopants by comparing their valence states and ionic size with those of Cu^{2+} (0.72Å). Group IA elements Li^{1+} (0.60Å), and Na^{1+} (0.95Å) are considered as *p*-type dopants (acceptors), and group IIIA elements Al^{3+} (0.50Å), Ga^{3+} (0.62Å) and In^{3+} (0.81Å), group IVB elements Ti^{4+} (0.68Å), Zr^{4+} (0.80Å) and Hf^{4+} (0.79Å) are selected as potential *n*-type dopants (donors). The dopant solubility is analysed by calculating their formation energies and the preferred growth conditions for both *p*-type and *n*-type dopants are discussed. We also analyze the trends in dopant energy levels and find the relationship between donor/acceptor levels and electronegativity. Therefore, our

calculation results can serve as experimental guideline and reference.

4.2 Computational Method and Formalism

The calculations in this study are conducted using the LSDA+U approach. An antiferromagnetic spin ordering is assumed for CuO [85]. The strong localized Cu 3d electrons are treated by using the Hubbard $U_{\text{eff}} = 7.5$ eV following Dudarev's approach [78]. The project-augmented wave (PAW) pseudopotentials are adopted, and Cu $3d^{10} 4s^1$ and O $2s^2 2p^4$ are treated as the valence electrons. For the calculations of extrinsic dopants, Li $1s^2 2s^1$, Na $2p^6 3s^1$, Al $3s^2 3p^1$, Ga $4s^2 3d^{10} 4p^1$, In $5s^2 4d^{10} 5p^1$, Ti $3p^6 4s^2 3d^2$, Zr $4s^2 4p^6 5s^2 5d^2$, and Hf $5p^6 6s^2 6d^2$, are treated as valence electrons. An energy cutoff of 600 eV is used for all the calculations.

Figure 4.1: Schematic illustration of the 2x3x2 CuO supercell used in this study.

Based on the calculated lattice parameters of CuO unit cell listed in Table 3.1, a 2x3x2 supercell with 96 atoms is shown in Figure 4.1, which is built for modelling of point defects and dopants. The lattice constants of the supercell are $a = 9.12 \text{ \AA}$, $b = 9.81 \text{ \AA}$ and $c = 9.92 \text{ \AA}$. Removing one Cu/O atom forms a Cu/O vacancy, and replacing one Cu atom with one external atom forms a substitution defect, whose ratio in this supercell is $\sim 1.04\%$. In all calculations, the volume and lattice parameters are fixed, while all atoms are allowed to relax until the Hellman-Feynman forces are less than $10 \text{ meV/\AA}$. The self-consistent total energy is converged to be less than 5 meV for all supercells. Due to large size of the supercell, less k points are needed for k -space integration. A 3x3x3 k -point mesh is enough for the supercell calculations.

The thermodynamic equilibrium concentration c of a defect or impurity can be evaluated by using the Boltzmann factor:

$$c = N_{site} \exp(-E_f^q / kT) \quad (4-1)$$

where N_{site} is the number (density) of available lattice sites, and E_f^q is the defect formation energy, which are calculated using the total energy, as well as the atomic/electron chemical potentials, according to the following equation:

$$E_f^q = E_{defect}^q - E_{perfect} + \sum_i n_i \mu_i + qE_F \quad (4-2)$$

where E_{defect}^q and $E_{perfect}$ are the total energy of the defected supercell in charge state q and the perfect supercell, respectively. μ_i denotes the corresponding atomic chemical potential, and n_i is the number of atoms that are removed ($n_i > 0$) or added ($n_i < 0$) to the supercell. E_F is the electron chemical potential or the Fermi level of CuO, which can

vary across the band gap of CuO. *In principle, the free energy should be used in Eq. (1). By using the zero-temperature formation energy, the contributions from vibrational entropy are ignored. These entropy contributions are usually small enough not to affect the qualitative results.*

In the case of one Cu/O atom being removed from the supercell, the formation energy of copper vacancy or oxygen vacancy in charge state q is therefore expressed as:

$$E_f^q = E_{defect}^q - E_{perfect} + \mu_{Cu/O} + qE_F \quad (4-3)$$

If one Cu atom is replaced by one extrinsic dopant atom, the formation energy of the dopant is expressed as:

$$E_f^q = E_{defect}^q - E_{perfect} + \mu_{Cu} - \mu_D + qE_F \quad (4-4)$$

Here μ_{Cu} , μ_O , and μ_D are the chemical potential of copper, oxygen and external dopant, respectively.

Because the total energy of a charged supercell does not converge, a uniform background charge is therefore added to the system to neutralize the net charge and make the total energy converge, which however introduces an additional interaction between the charge and its image. This image charge interaction is pseudo, which however depends on the supercell size and can be reduced by using a large supercell. The total energy for a charged supercell can be corrected using the Makov and Payne method [62, 63],

$$\Delta E_{mp} = + \frac{q^2 \alpha_M}{2\epsilon L} + \frac{2\pi q Q}{3\epsilon L^3} + O(L^{-5}) \quad (4-5)$$

Here, α_M is the lattice-dependent Madelung constant and L is the size of the supercell.

ε is the static dielectric constant of CuO and Q is quadrupole moment. Typically, the last two terms decay rapidly as the supercell size and can be ignored due to their very small contributions to the total energy. Therefore, only first monopole term is adopted in the practical total energy correction of a charged supercell. In our model, the experimental dielectric constant of CuO is 18 as taken from ref. 89.

4.3 Calculations of Atomic Chemical Potentials

As from Equation (4-2), (4-3), and (4-4), the formation energies should depend on the atomic chemical potentials that can be tuned by changing the growth conditions. To maintain the stability of CuO with respect to O_2 gas and metallic Cu, the chemical potentials of Cu and O must satisfy the following relationship in order to coexist with CuO:

$$\mu_{Cu} + \mu_O = \mu_{CuO} \quad (4-6)$$

here, μ_{CuO} is the chemical potential of bulk CuO, which should be a constant and calculated as the total energy of per CuO unit formula.

The upper bound of μ_O denoted by μ_O^0 (corresponding to O rich growth conditions) is set by the total energy of isolated oxygen molecular ($\mu_O^0 = \frac{1}{2}\mu_{O_2}$), which is calculated by placing one O_2 molecule in a periodic cubic box with the size of 20 Å and by using the Gamma point only in the k -space integration. The calculated O-O bond length is 1.20 Å, consistent with experimental value of 1.21 Å as shown in Table 4.1.

Table 4.1: Comparison of the theoretical lattice parameters with experimental values for Cu, Cu₂O, and O₂.

	Cu (Fm-3m)	Cu ₂ O (Pn-3m)	1/2 O ₂
Lattice constant	a	a	Bond length
This work (Å)	3.47	4.11	1.20
Experiment (Å)	3.61	4.27	1.21

The lower bound of oxygen chemical potential is set by the formation of Cu₂O,

$$2\mu_{\text{Cu}} + \mu_{\text{O}} \leq \mu_{\text{Cu}_2\text{O}} \quad (4-7)$$

Combining equation (4-6) and (4-7) yields:

$$\mu_{\text{O}} \geq 2\mu_{\text{CuO}} - \mu_{\text{Cu}_2\text{O}} \quad (4-8)$$

Here, $\mu_{\text{Cu}_2\text{O}}$ is the chemical potential of bulk Cu₂O, which has a cubic structure. Since the computed total energy of a system depends on both the different exchange-correlation functional and the value of Hubbard U parameter, we also calculate the properties of Cu₂O using the same method as we do for CuO. Therefore, we can compare the total energy difference between two different copper oxides. The computed lattice constant for Cu₂O is 4.11 Å as shown in Table 4.1, which differs from the experimental value slightly [90]. Therefore, the lower limit of oxygen chemical potential computed using equation (4-8) is equal to $\mu_{\text{O}}^0 - 1.94$ eV, corresponding to O poor growth conditions.

We have computed the properties of metallic Cu using both the LDA and LDA+U approaches. The computed lattice constant obtained using LDA is 3.52 Å, similar to that of 3.47 Å obtained using LDA+U approach. However, the computed chemical potential for metallic Cu denoted as μ_{Cu}^0 differs by more than 2 eV between the two methods. To

be consistent with the chemical potential of CuO, we therefore use the values obtained by LDA+U approach as shown in Table 4.1. Thus, we can express the chemical potential range of Cu to be between $\mu_{\text{Cu}}^0 - 0.1$ eV and $\mu_{\text{Cu}}^0 - 2.04$ eV. The computed formation enthalpy of CuO is -2.04 eV, slightly lower than the experimental value of -1.62 eV [91].

Table 4.2: The computed upper-limit of the chemical potentials for all dopants that we have examined ($\mu_{\text{D}} - \mu_{\text{D}}^0$). All units are in eV.

	Li	Na	Al	Ga	In	Ti	Zr	Hf
O rich	-3.2	-2.18	-8.74	-5.65	-4.94	-10.32	-11.37	-12.08
O poor	-2.23	-1.22	-5.83	-2.74	-2.03	-6.44	-7.49	-8.2

The chemical potentials of dopants need to satisfy some constraints to avoid the formation of dopant-related secondary phases. Since the dopants in this study are all metals, the formation of dopant oxides should be avoided by controlling the dopant chemical potential. For example, for Al doping, the chemical potential of Al should satisfy:

$$\mu_{\text{Al}} \leq \mu_{\text{Al}}^0 \text{ and } 2\mu_{\text{Al}} + 3\mu_{\text{O}} \leq \mu_{\text{Al}_2\text{O}_3} \quad (4-9)$$

Here, μ_{Al}^0 is the total energy of metallic Al (μ_{D}^0 for other dopants in metallic phase), and $\mu_{\text{Al}_2\text{O}_3}$ is the total energy of Al_2O_3 . The computed lattice constants for all dopants in both metallic and oxide phases are shown in Table 4.3, in good agreement with the experimental values. We list the upper-limit chemical potential of dopants ($\mu_{\text{D}} - \mu_{\text{D}}^0$) in Table 4.2, under two different growth conditions.

Table 4.3: Comparison of the theoretical lattice parameters with experimental values [91] for dopants in both metallic and oxide phases. ΔH_f is the formation enthalpy of the oxide compounds.

	Li ₂ O		Li	Na ₂ O		Na
	(Fm-3m)		(Im-3m)	(Fm-3m)		(Im-3m)
	$a(\text{\AA})$	ΔH_f (eV)	$a(\text{\AA})$	$a(\text{\AA})$	ΔH_f (eV)	$a(\text{\AA})$
This work	4.51	-6.20	3.36	5.42	-4.30	4.05
Experiment	4.60	-6.40	3.51	5.55	-4.37	4.29

	α -Al ₂ O ₃ (R-3C)			Al (Fm3m)
	$a(\text{\AA})$	α	ΔH_f (eV)	$a(\text{\AA})$
This work	5.10	55.27	-17.47	3.99
Experiment	5.13	55.36	-17.40	4.05

	β -Ga ₂ O ₃ (C2/m)					Ga (Bmab)		
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	ΔH_f (eV)	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$
This work	12.12	3.02	5.77	103.75	-11.29	4.43	4.44	7.48
Experiment	12.23	3.04	5.80	103.7	-11.30	4.51	4.52	7.65

	In ₂ O ₃ (Ia-3)		In (I4/mmm)	
	$a(\text{\AA})$	ΔH_f (eV)	$a(\text{\AA})$	$c(\text{\AA})$
This work	8.71	-9.87	3.19	4.85
Experiment	8.74	-9.60	3.25	4.95

	rutile-TiO ₂ (P42/mnm)			Ti (3/mmc)	
	$a(\text{\AA})$	$c(\text{\AA})$	ΔH_f (eV)	$a(\text{\AA})$	$c(\text{\AA})$
This work	4.56	2.92	-10.32	2.86	4.52
Experiment	4.59	2.96	-9.80	2.95	4.69

	ZrO ₂ (P21/c)					Zr (3/mmc)	
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	ΔH_f (eV)	$a(\text{\AA})$	$c(\text{\AA})$
This work	5.12	5.22	5.27	99.67	-11.37	3.15	5.10
Experiment	5.15	5.21	5.31	99.23	-11.40	3.23	5.15

	HfO ₂ (P21/c)					Hf (3/mmc)	
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	ΔH_f (eV)	$a(\text{\AA})$	$c(\text{\AA})$
This work	5.03	5.12	5.20	99.60	-12.08	3.12	4.94
Experiment	5.20	5.17	5.30	99.18	-11.60	3.20	5.06

4.4 Computed Results and Discussion

4.4.1 Formation Energies of Intrinsic Vacancies

In this part, we discuss the formation energies of copper and oxygen vacancies under two limiting growth conditions (oxygen rich and oxygen poor). We also consider the vacancies with different charged states. Computed formation energies of the intrinsic vacancies as functions of the Fermi level are shown in Figure 4.2. The Fermi level is considered to vary from the top of the valence band to the bottom of the conduction band. The slope of the lines in the figure is equal to the charge state of vacancies. The intersections of lines correspond to transitions between two different charged states, where the formation energies of the vacancy for the two charge states are equal. The Fermi level value at the intersection point is called the charge transition energy level, which is related to the ionization energy of defects.

Under oxygen poor growth condition shown in Figure 4.2 (a), if the Fermi level is below 0.76 eV, the neutral oxygen vacancy has the lowest formation energy and is the dominant defect. If the Fermi level is above 0.76 eV, the copper vacancy with -2 charge state has the lowest formation energy and becomes the most dominant defect. Among the 0, +1 and +2 charge states of oxygen vacancy, the formation energy of neutral oxygen vacancy is the lowest in the whole range of Fermi level. And the charge transition energy levels of oxygen vacancy are very far from the conduction band, indicating that oxygen vacancy should be a deep donor and cannot emit a significant amount of electrons to make CuO *n*-type. On the other hand, the formation energies of both -1 and -2 charged

copper vacancies are very high under oxygen poor condition. Therefore, p -type conduction should be very weak under oxygen poor condition.

Figure 4.2: The calculated formation energies of intrinsic vacancies as functions of the Fermi level under: (a) O-poor condition, and (b) O-rich condition. While all the states of oxygen vacancy are shown, only the lowest formation energy states of copper vacancy are shown.

Under the oxygen rich condition shown in Figure 4.2 (b), the formation energies of -1 and -2 charged copper vacancies are always lower than that of oxygen vacancy across the full range of Fermi level. On the other hand, the formation energy of neutral copper vacancy is always higher than those of charged copper vacancies, indicating that copper vacancy should be a shallow acceptor, whose (-1/-2) transition energy level locates at 0.2 eV above the top of the valence band. Our results can not only explain the experimentally observed p -type conduction in CuO [20-22], but also provide a way to suppress the formation of copper vacancy, which may kill the electrons generated by n -type doping.

4.4.2 Formation Energies of Group IA Acceptor Dopants (Li and Na)

The formation energies of group IA acceptors under the oxygen rich and oxygen poor conditions are shown in figure 4.3 as functions of Fermi levels, respectively. The formation energies of intrinsic vacancies are also shown in the figure for comparison. For a given Fermi level, only the charge state that has the lowest formation energy is plotted in the figure. The computed formation energies of Li and Na are very similar for both oxygen rich and poor conditions.

Under oxygen poor growth condition, the formation energies of Li and Na dopants are lower than those of the intrinsic vacancies. The -1 charged state of Li_{Cu} is more stable than its neutral charge state in a wide range of Fermi levels. Similarly, the -1 charged state of Na_{Cu} is more stable than its neutral charge state if the Fermi level is larger than 0.09 eV. Thus, the (0/-1) transition energy level for Li and Na dopants are 0.03 eV and 0.09 eV, respectively, very close to the top of valence band, indicating that both Li and Na are shallow acceptors, especially for Li dopant.

Under oxygen rich growth condition, the formation energies of Li and Na dopants are even lower than those under oxygen poor condition, which are negative throughout the range of Fermi level. Therefore, Li and Na can spontaneously substitute Cu atoms under oxygen rich condition. The -1 charged Li and Na dopants can emit enough “holes” to the CuO valence band due to the shallow acceptor levels, contributing to *p*-type CuO. Thus, the *p*-type conduction of CuO can be further enhanced by both Li and Na doping. Experimentally, it was indeed observed that Li-doped CuO single crystal shows

improved p -type conductivity by up to two orders of magnitude [21].

Figure 4.3: The calculated formation energies of group IA acceptors, Li and Na, as functions of the Fermi level under: (a) O-poor condition and (b) O-rich condition.

4.4.3 Formation Energies of Group IIIA Donor Dopants (Al, Ga and In)

The formation energies of group IIIA donors under both oxygen rich and oxygen poor conditions are shown in figure 4.4 as functions of the Fermi levels. From figure 4.4, it is found that the formation energies of Al, Ga, and In dopants under oxygen poor condition are much lower than those under oxygen rich condition. Also, under oxygen rich condition, the formation energy of charged copper vacancy is lower than those of the dopants, which can act as an electron killer and affect the n -type doping efficiency. Thus, the oxygen poor growth condition can not only facilitate the solubility of group IIIA dopants in CuO but also suppress the formation of copper vacancy, both of which can benefit the n -type doping. The formation energy of Ga dopant is smaller than those of Al

and In dopants under both oxygen rich and oxygen poor conditions. The average Al-O, Ga-O, and In-O bond lengths after relaxation are 1.84 Å, 1.91 Å, and 2.10 Å, respectively, as compared with the Cu-O distance of 1.89 Å. Therefore, the lattice distortion is in the decreasing order of In, Al and Ga dopants. That is why Ga dopant has the lowest formation energy and largest solubility in CuO, while In dopant is contrary.

As shown in figure 4.4, there are two possible charge states, 0 and +1 for group IIIA donors in CuO across the full range of Fermi levels. The +1 charged group IIIA dopants which contribute one electron to the conduction band, are stable at low Fermi levels and become unstable at high Fermi levels. The position of transition energy level with respect to the conduction band minimum for donor dopant is essential for effective *n*-type doping. The (0/+1) transition energy level for Al dopant locates at 0.51 eV below the conduction band bottom, and therefore neutral Al_{Cu} should be more stable in *n*-type CuO than charged one. The high ionization energy of Al_{Cu} makes it hard to excite the electron on the deep donor level to the conduction band of CuO at room temperature. Our result is consistent with the experimental finding that *n*-type conduction is not observed by Al doping [21]. The (0/+1) transition energy level for Ga dopant is at 0.42 eV below the conduction band bottom, which is also too deep to be ionized at room temperature and to contribute electrons to the conduction band. However, the donor level of In dopant is shallower compared with Al and Ga, which is at 0.3 eV below the conduction band bottom. It is found that the ionization energy decreases from Al, Ga, to In, because the atomic orbital energy level increases from Al, Ga to In.

Figure 4.4: The calculated formation energies of group IIIA donors (Al, Ga, and In), as functions of the Fermi level under: (a) O-poor condition and (b) O-rich condition.

4.4.4 Formation Energies of Group IVB Donor Dopants (Ti, Zr and Hf)

The formation energies of group IVB donors under both oxygen rich and oxygen poor conditions are shown in figure 4.5 as functions of the Fermi levels. Similarly as group III donors, the computed formation energies of group IVB donors under oxygen poor condition is lower than those under oxygen rich condition. Besides, the formation energy of Ti dopant is smaller than those of Zr and Hf dopants for both oxygen rich and oxygen poor conditions. It is found that Ti doping in CuO causes smaller lattice distortion than Zr and Hf dopants. Also, the computed formation energies of Zr and Hf dopants are very close due to their similar ionic sizes as shown in Table 4.4.

In figure 4.5, there are three possible charge states, 0, +1, and +2 for group IVB donors in the CuO band gap. It is possible for these dopants to contribute two excess valence electrons to the CuO conduction band. At low Fermi levels, the formation energies of the

+2 charged dopants are lower than other charge states, indicating they are stable in *p*-type CuO. However, they become unstable in *n*-type CuO. The calculated (0/+1) transition energy level for Ti dopant is very far from the conduction band bottom, implying that Ti is a deep donor in CuO. The (0/+1) transition energy levels for Zr and Hf are relatively shallower at 0.20 eV and 0.19 eV below the conduction band bottom, respectively. It is therefore possible to excite some of the excess valence electrons from both Zr and Hf dopants to the CuO conduction band at room temperature, which contributes to *n*-type CuO. However, the formation energies of both Zr and Hf dopants are very high even under oxygen poor condition. The low solubility of Zr and Hf dopants can limit the dopant concentrations in CuO and therefore affect the electron carrier concentrations.

Figure 4.5: The calculated formation energies of group IVB donors (Ti, Zr, and Hf), as functions of the Fermi level under: (a) O-poor condition, and (b) O-rich condition.

Table 4.4: Ionic radius ($\text{\AA}$) and Pauling electronegativity of the tested dopants. The ionic radius of Cu^{2+} is $0.72 \text{ \AA}$.

	Li^{1+}	Na^{1+}	Al^{3+}	Ga^{3+}	In^{3+}	Ti^{4+}	Zr^{4+}	Hf^{4+}
Ionic radii ($\text{\AA}$)	0.6	0.95	0.50	0.62	0.81	0.68	0.8	0.79
Electronegativity	0.98	0.93	1.61	1.81	1.78	1.54	1.33	1.3

4.5 Trends in Transition Energy Levels

To analyse the trends in the ionization energies of various dopants, we summarize the calculated donor and acceptor levels for all tested dopants in figure 4.6. For both group IIIA and IVB donor dopants, it is found that the ionization level generally decreases as atomic number increases within the same group. This systematic variation could be explained by the electronegativity of the dopants. Because the Pauling electronegativity of Ti is 1.54, higher than 1.33 for Zr and 1.3 for Hf, Ti atom attracts electrons more strongly and requires higher energy to be ionized. The same behaviour is found for group IIIA Al, Ga, and In dopants. Oppositely, Li is slightly more electronegative than Na, and thus the acceptor level of Li is lower than that of Na.

Figure 4.6: Ionization levels in the band gap for the dopants in CuO. VBM denotes valence band maximum and CBM represents conduction band minimum.

4.6 Summary

In summary, we have calculated the formation energies of intrinsic vacancies and extrinsic dopants in CuO using first-principles DFT calculations. The defect transition energy levels as well as the most stable defect types under various growth conditions are discussed and the suitable *p*-type and *n*-type dopants are suggested by analysing the trends in transition energy levels.

(1) For intrinsic vacancies, we find that under oxygen rich condition, copper vacancy can easily form due to the very low formation energy. However, under oxygen poor condition and *p*-type CuO, neutral oxygen vacancy is the most stable defect. Moreover, it is found that copper vacancy has stable charge states of -1 and -2 under oxygen rich condition. Therefore, we conclude that copper vacancy is a shallow acceptor and can make CuO *p*-type under oxygen rich condition, in agreement with experimental observations.

However, oxygen vacancy is a deep donor and should not contribute to *n*-type conduction. For *n*-type doping, it is necessary to limit the formation of copper vacancy by adopting oxygen poor growth condition.

(2) For group IA acceptors, we find that the formation energies of Li and Na dopants are negative under oxygen rich condition, which implies that Li and Na dopants have high solubility in CuO. Moreover, the ionization levels of Li and Na dopants are 0.03 eV and 0.09 eV, respectively, which are shallow enough to contribution holes to the valence band at room temperature. Therefore, the *p*-type conduction in CuO can be further enhanced by Li and Na doping, especially for Li doping, which is consistent with the experimental findings.

(3) To obtain better *n*-type performance, CuO should be prepared under oxygen poor condition where the group IIIA and IVB donors have lower formation energies than under oxygen rich condition. We also find that the donor levels of Al, Ga, and Ti are too far from the conduction band, indicating that they are deep donors and difficult to contribute to *n*-type conduction in CuO. Comparatively, In dopant has the shallowest donor level of 0.3 eV below the CBM among the group IIIA dopants, while Zr and Hf are calculated to have donor levels around 0.2 eV below the CBM, which are shallower than Ti. On the other hand, the formation energy of -2 charged copper vacancy is lower than those of In, Zr and Hf dopants when the Fermi levels are close to the CBM even under oxygen poor condition. Although the formation of copper vacancy can be suppressed by adopting oxygen poor growth conditions, the solubilities of donor dopants are not high

enough to completely compensate the hole carriers generated by copper vacancies, which is essential for *n*-type doping in CuO. Our results have indicated that *n*-type doping in CuO is very difficult to achieve under thermodynamic equilibrium conditions.

(4) In summary, it is observed that the acceptor and donor levels are closely related to the electronegativity of dopants. For donor dopants in the same group, the donor level decreases as the atomic number increases. This is because atoms with smaller atomic numbers are more electronegative than those with larger atomic numbers. Therefore, for *n*-type doping, it is favourable to use less electronegative elements. On the contrary, for *p*-type doping, it prefers to use more electronegative dopants. For example, Li is more electronegative than Na, and thus its acceptor level is shallow than that of Na.

Chapter V Defect Complexes in CuO

5.1 Introduction

Our study has shown that it is relatively easy to obtain *p*-type conductivity in CuO, but *n*-type CuO is very difficult to achieve because single *n*-type dopants either have deep donor levels or limiting solubility. They are inefficient in generating free electrons at room temperature. Among group-III elements, Ga has the most similar size to Cu. However, it only produces a deep donor level in CuO, which is not desirable for *n*-type doping. Although Zr, Hf, and In are suggested to be relatively shallow donor dopants in CuO, their ionization energies of 0.2-0.3 eV are still not low enough to be easily ionized at room temperature ($k_B T \sim 0.03$ eV). Accompanied by the limited thermodynamic solubility of these dopants, it is thus very challenging to produce *n*-type CuO.

In an effort to resolve this issue, we notice that there are experimental evidences of shallow defect levels being produced by donor-acceptor (*n-p*) codoping in other systems such as ZnO [92-95] and GaN [96]. Theoretically, Yamamoto *et al.* first proposed codoping with acceptor and donor (2:1 for *p*-type and 1:2 for *n*-type) to realize low-resistivity *p*-type ZnO and GaN [114, 115]. In this case, defect association occurs due to the Columbic attraction between *n*- and *p*-type dopants with opposite charges [97-99]. Several theoretical studies have been performed to elucidate the underlying mechanism of increased conductivity in codoped samples. The effect of wavefunction interaction between the *n*- and *p*-type dopants on the defect levels has been verified by

theoretical calculations [100-104]. It is noted that the change of electronic structure upon codoping can affect the electrical properties. Therefore, Yan *et al.* explained the experimentally observed shallow acceptor/donor levels with the change of valence band and/or conduction band edges by the impurity bands formed in the gap upon codoping [105]. It is also noted that *n-p* codoping approach has been intensively utilized in engineering the band structure of wide-gap semiconductors [106-113]. The solubility of dopants may also be enhanced through codoping. Interstitial H or Li donor codoping can increase the concentration of Mn acceptor in GaAs, and can subsequently be removed by thermal annealing [116, 117]. Katayama-Yoshida *et al.* proposed to overcome the low solubility of codopants by the spinodal nano-decomposition method [118]. However, there is little literature report on *n-p* codoping in CuO, which we will address in this chapter.

Figure 5.1: The codoping mechanism: (1) the donor-acceptor level repulsion lowers the acceptor level and raises the donor level (left), (2) the impurity band may reduce electron or hole activation energy (right). The two figures are from ref. 92.

In this theoretical study, we examine the effect of n - p codoping on reducing the donor ionization energy in CuO using first-principle density functional theory (DFT) calculations, which is very important for fabrication of highly conductive n -type CuO and realization of CuO p - n junction solar cells. Two kinds of acceptor dopants which are N on O site and Li on Cu site are selected. And two types of donor dopants are selected, which are relatively shallow donors Zr and In and relatively deep donors Al and Ga. We have conducted extensive calculations on different combinations of donor and acceptor, and only presented the important results on N codoping with Zr and In, and Li codoping with Al/Ga. We compute the formation energies and transition energy levels for possible n -type complexes and compare the results with those of single n -type dopants. Other donor and acceptor combinations are also tested, which are discussed at the end of this chapter.

5.2 Computational Method

First-principles DFT calculations are conducted using the VASP code. The PAW pseudopotentials are used, while Cu $3d$, $4s$, O $2s$, $2p$ and dopants' outmost s , p , d orbitals are treated as the valence electrons. An energy cutoff of 600 eV for the plane wave expansion is used in all calculations. The LSDA+U method ($U_{\text{eff}}=7.5$ eV for Cu $3d$ electrons) is adopted following the Dudarev's approach. An antiferromagnetic spin ordering is assumed for CuO. A $2 \times 3 \times 2$ 96-atom supercell is built to simulate various defects based on theoretical lattice parameters. A gamma centered $3 \times 3 \times 3$ k -point mesh for the Brillouin zone of supercell is employed. A refined $4 \times 4 \times 4$ k -point mesh is used for

the density of states plots. In all calculations, all the atoms are allowed to relax until the force on atoms is smaller than 0.02 eV/Å.

The formation energy of a defect complex in CuO is defined as

$$E_f = E_{doped} - E_{perf} - n\mu_{dopant} + m\mu_{Cu/O} + qE_F \quad (5-1)$$

where E_{doped} is the total energy of the supercell with dopants, E_{perf} is the total energy of a perfect supercell, n is the number of dopant atoms, m is the number of Cu or O atoms being removed from the supercell, μ_{dopant} is the chemical potential of dopant, $\mu_{Cu/O}$ is the chemical potential of Cu or O, q is the charge state of the defect and E_F is the Fermi energy of the system. The image charge error due to the finite size of supercell is corrected by using the monopole term in the Makov-Payne (MP) scheme, whose value is very small due to the large dielectric constant of CuO ($\epsilon=18$). The detailed calculations of chemical potentials of Cu, O, and metal dopants under two extreme growth conditions can be found in section 4.3. We use nitrogen gas as doping source: $\mu_N \leq \frac{1}{2}\mu_{N_2}$ and $\mu_{In} + \mu_N \leq \Delta H_f(InN)$ (for In and N codoping).

5.3 N Acceptor Codoping with Zr and In

5.3.1 Calculation Model and Binding Energies

In our model, one Zr dopant occupies the nearest Cu site of the N acceptor, forming the $Zr_{Cu}-N_O$ *n*-type defect complex as shown in figure 5.2(a). Similarly, one In dopant occupies the nearest Cu site of the N acceptor, forming the $In_{Cu}-N_O$ passive complex, and two In dopants occupy the nearest Cu sites of the N acceptor, forming the $2In_{Cu}-N_O$ *n*-type complex as shown in figure 5.2(b), where the In-In distance is almost twice as

long as the In-N distance.

Figure 5.2: The calculation models for (a) $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ n -type complex, and (b) $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ n -type complex.

To verify if the complex can form in CuO, we calculated the binding energy between Zr and N using:

$$E_b = E_{\text{tot}}(\text{Zr}_{\text{Cu}} - \text{N}_{\text{O}}) + E_{\text{tot}}(\text{CuO}) - E_{\text{tot}}(\text{Zr}_{\text{Cu}}) - E_{\text{tot}}(\text{N}_{\text{O}}) \quad (5-2)$$

where E_{tot} is the total energy of the supercells. According to equation (5-1), the binding energy can also be written as:

$$E_b = E_f(\text{Zr}_{\text{Cu}} - \text{N}_{\text{O}}) - E_f(\text{Zr}_{\text{Cu}}) - E_f(\text{N}_{\text{O}}) \quad (5-3)$$

where E_f is the formation energy of the dopants. A negative binding energy indicates that the complex is stable energetically, and thus the acceptor is more likely to form complexes with the donor. The calculated binding energies are listed in Table 5.1. The negative binding energy at -0.39 eV indicates that $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ is stable with respect to the isolated defects and is likely to form in CuO. The binding energy for $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ is calculated between $\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ and In_{Cu} using the following relation:

$$E_b = E_f(2\text{In}_{\text{Cu}} - \text{N}_{\text{O}}) - E_f(\text{In}_{\text{Cu}}) - E_f(\text{In}_{\text{Cu}} - \text{N}_{\text{O}}) \quad (5-4)$$

which is small at -0.1 eV, indicating that $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ is not very stable at high temperatures.

Table 5.I: Calculated binding energies, E_b , of N-related defect complexes in neutral charge state in CuO. Doping type i means passive doping. All energies are in eV.

Reaction	Type	E_b
$\text{Zr}_{\text{Cu}} + \text{N}_{\text{O}} \rightarrow \text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$	n	-0.39
$\text{In}_{\text{Cu}} + \text{N}_{\text{O}} \rightarrow \text{In}_{\text{Cu}}\text{-N}_{\text{O}}$	i	-0.85
$\text{In}_{\text{Cu}} + \text{In}_{\text{Cu}}\text{-N}_{\text{O}} \rightarrow 2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$	n	-0.10

5.3.2 Formation Energies and Transition Energy Levels

The formation energies of N codoping with Zr and In are shown in figure 5.3 as functions of the Fermi levels. The calculated formation energies of Zr and In single dopants are also shown for comparison. The Fermi level (E_F) varies from 0 eV at the VBM to 1.32 eV at the CBM. The transition energy levels between different charge states are denoted as the solid dots in the figure. For $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ and $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$, there are two possible charge states (0 and +1) in the gap. The slop of the lines indicates the charge state. It is found that the (0/+1) transition energy level of $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ locates at 0.15 eV below the CBM, slightly shallower than the (0/+1) transition energy level of single Zr_{Cu} dopant, due to the mutual interaction between Zr and N codopants. Also, $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ is found to have a shallower donor level than single In_{Cu} dopant, which is at 0.16 eV below the CBM. All dopants have much lower formation energies under O poor condition than under O rich condition. However, the formation energies of the N-related n -type

complexes are even higher than those of single donor dopants, which will lead to a low concentration of n -type complexes in CuO under thermal equilibrium condition. However, this issue may be resolved by using non-equilibrium growth methods such as pulsed laser deposition, MBE, MOCVD and MOVPE.

Figure 5.3: Formation energies of N codoping with Zr and In as functions of Fermi levels, in the O-poor and O-rich conditions, respectively. The formation energies of Zr and In single dopants are also shown for comparisons.

We also discuss the possibility to form meta-stable $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ and $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ complexes in CuO, as proposed in ref. 118 by using the spinodal nano-decomposition method. We noticed that, based on the calculated Zr-N binary phase diagram [119], it is unlikely to initiate the spinodal nano-decomposition in the $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ codoping as that reported in the Ga-N system [118], due to three reasons: (a) the DFT calculated binding energy is -0.39

eV at 0 K which is not expected to reach a large positive value needed for spinodal decomposition at the higher synthesis temperatures, (b) the calculated liquidus line is not flat enough to expect a spinodal decomposition, (c) the two solid phases at N-rich and Zr-rich sides are of different crystal structures which makes it difficult to form spinodal structures. *However, similar to the Ga-N system [120], these $2\text{In}_{\text{Cu}}\text{-N}_\text{O}$ complexes may undergo spinodal nano-decomposition into N-rich and N-poor phases and result in high concentration of $2\text{In}_{\text{Cu}}\text{-N}_\text{O}$ complexes in CuO.*

Figure 5.4: The Zr-N phase diagram at 101,325 Pa as from ref. 119.

5.4 Li Acceptor Codoping with Al and Ga

5.4.1 Calculation Model and Binding Energies

In our model, one or two Al/Ga dopants occupy the nearest Cu sites of the Li acceptor, forming the $\text{Al}_{\text{Cu}}/\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ passive complexes or the $2\text{Al}_{\text{Cu}}/2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ *n*-type complexes, in which two donor dopants are separated from each other as shown in figure 5.5.

Figure 5.5: The calculation models for (a) $\text{III}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ *passive* complex and (b) $2\text{III}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ *n-type* complex, where $\text{III}=\text{Al}$, Ga , and In .

The binding energies for $\text{Al}_{\text{Cu}}/\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ are calculated according to:

$$E_b = E_f(\text{Al}_{\text{Cu}} - \text{Li}_{\text{Cu}}) - E_f(\text{Al}_{\text{Cu}}) - E_f(\text{Li}_{\text{Cu}}) \quad (5-5)$$

which are as large as -1.16 eV and -1.37 eV, respectively, as shown in Table 5.2, and therefore they are very likely to form in CuO. The large binding energies can be explained as follows. To form the defect complex, Al_{Cu} or Ga_{Cu} transfers one of its electrons to Li_{Cu} , forming neutral defect complexes, which lowers than total energy of the CuO system and leads to the Coulomb interaction between Li_{Cu}^- and Al_{Cu}^+ or Ga_{Cu}^+ . It is noted that the calculated binding energies decrease as the separation between donor and acceptor increases to about 6.0 Å. Thus the nearest complexes are the most stable configurations.

Table 5.2: Calculated binding energies and formation energies of Li-related passive complexes in CuO at different donor and acceptor distances (d).

Complex	d (Å)	E_b (eV)	E_f (eV)
Li _{Cu} -Al _{Cu}	2.85	-1.16	0.70
Li _{Cu} -Ga _{Cu}	2.82	-1.37	0.32
Li _{Cu} -In _{Cu}	2.84	-1.45	0.74
Li _{Cu} -Al _{Cu}	6.0	-0.93	0.93
Li _{Cu} -Ga _{Cu}	6.0	-1.11	0.58

Table 5.3: Calculated binding energies, formation energies in neutral charge states and transition energy levels for Li-related n -type complexes in CuO; E_C is the conduction band edge of pure CuO. All energies are in eV. NA is not calculated.

Complex	E_b	(0/+1)	E_f	
			O-poor	O-rich
Al _{Cu}		$E_C - 0.51$	1.02	1.99
Li _{Cu} -2Al _{Cu}	-0.32	$E_C - 0.37$	1.40	2.37
Ga _{Cu}		$E_C - 0.42$	0.85	1.82
Li _{Cu} -2Ga _{Cu}	-0.2	$E_C - 0.34$	0.97	1.94
In _{Cu}		$E_C - 0.30$	1.35	2.32
Li _{Cu} -2In _{Cu}	0.18	NA	2.27	3.24

The binding energies of n -type complexes are calculated between one Al/Ga and one passive complex following the relation:

$$E_b = E_f(2\text{Al}_{\text{Cu}} - \text{Li}_{\text{Cu}}) - E_f(\text{Al}_{\text{Cu}}) - E_f(\text{Al}_{\text{Cu}} - \text{Li}_{\text{Cu}}) \quad (5-6)$$

which are also negative at -0.32 eV and -0.2 eV, respectively. Therefore, the n -type

complexes are energetically stable and can form if more donors are doped into CuO than Li acceptors. However, the calculated binding energy between one In and one $\text{In}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is positive at 0.18 and the $2\text{In}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ *n*-type complex is not stable in CuO. This is likely due to the large size of In atom as compared with Cu atom. So we will only discuss the Li and Al/Ga codoping subsequently.

5.4.2 Formation Energies and Transition Energy Levels

The formation energies of Li codoping with Al and Ga are shown in figure 5.6 as functions of the Fermi level, which are compared with those for Al and Ga single dopants in the same figure. From figure 5.6, it is clear that the formation energies of $\text{Al}_{\text{Cu}}/\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ passive complexes are the same under O-poor and O-rich conditions. The low formation energies indicate that the solubility of Al/Ga dopants could be enhanced by Li codoping. However, those passive complexes only have one neutral state in the gap and cannot contribute electrons to the materials. For *n*-type complexes, their maximum solubility in CuO is achieved under O-poor condition. Moreover, each *n*-type complex has two possible charge states (0 and +1) in the gap, which can donate one electron to the conduction band of CuO. It is found that the donor levels of $2\text{Al}_{\text{Cu}}/2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ are shallower than those of Al_{Cu} and Ga_{Cu} by 0.14 eV and 0.08 eV, respectively, because the level repulsion between donor and acceptor pushes the donor level closer to the conduction band minimum. Since the formation energy of $2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is very close to that of single Ga_{Cu} , excess Ga dopants can form either isolated defects (Ga_{Cu}) or *n*-type complexes with Li. Also, the formation energy of $2\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is not very high to constrain

its solubility. The formation energy is lower in Al_{Cu} than in $2\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$, because the complex needs more energy to incorporate three atoms into Cu sites simultaneously. However, the binding energy between codopants can help to decrease the formation energy. Therefore, Li codoping should be able to enhance the n -doping efficiency of Al and Ga dopant in CuO by decreasing the donor ionization energy.

Figure 5.6: Formation energies of Li codoping with Al and Ga as functions of the Fermi level under O-poor and O-rich conditions, respectively. The formation energies of Al and Ga single dopants are also shown for comparison.

5.4.3 Electronic Structures of Doping Complexes

Although the Al_{Cu} / $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ complexes are electrically passive and cannot provide either electron or hole in CuO, it may affect the electrical properties by modifying the electronic structure. We investigate the modified band structure of CuO with passive

complexes by calculating the total and partial DOS as shown in figure 5.7(a) and 5.7(b), respectively, for $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ in a 96-atom CuO supercell. From the total DOS, the basic band structure of codoped CuO remains the same as pure CuO. However, an empty impurity band is created near the CBM of CuO. For pure CuO, the CBM is determined by the Cu 3d states. From the partial DOS (PDOS), it is shown that the empty impurity band below the CBM is mainly composed of Cu 3d states and Al/Ga s and p states. Due to the lower orbital energy of Al 3s and 3p states, the empty impurity band for Al-Li codoping is somewhat deeper than that for Ga-Li codoping. *The density of states for $2\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and $2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ are very similar except that an extra occupied level is introduced in the band gap by the second Al or Ga donor.*

Figure 5.7: The total and partial density of states (DOS) of (a) $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and (b) $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ in a 96 atom CuO supercell. The dashed line is the total DOS for pure CuO.

Supercells of 96 atoms, 64 atoms, and 48 atoms containing one passive complex are adopted to simulate different codoping concentrations of 2.1%, 3.1%, and 4.2%,

respectively. The calculated total DOS for $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ at different concentrations are shown in figure 5.8. Here, the DOS in the different systems are aligned by referring to the core levels of the atoms far from the impurities. At a low concentration of 2.1% for Al/Ga, the empty impurity bands near the CBM of CuO reduce the band gap by -0.25 eV and -0.17 eV, respectively. At such low doping concentration, the impurity band is quite localized. From figure 5.4, as the doping concentration increases, the impurity band broadens and becomes dispersive.

Figure 5.8: The total density of states of (a) $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and (b) $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ codoped CuO at different concentrations of 2.1%, 3.1% and 4.2%, respectively. The vertical dotted line indicates the conduction band edge and the number nearby is the band gap value.

The calculated band structures for $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ at a high concentration of 4.2% in CuO are shown in figure 5.9 (a)-(b), respectively. At such high concentration, the band structures for Al and Ga codoping with Li are very similar to each other. The large curvature at the bottom of the conduction band indicates high electron carrier mobility, likely due to the hybridization between Cu $3d$ states and more delocalized sp states of Al/Ga, especially for Ga, in the impurity states.

Figure 5.9: Calculated band structures for (a) $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ and (b) $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ at a high concentration of 4.2% in CuO. The Fermi level of pure CuO is set at zero.

5.4.4 Donor ionization energies

The conduction band edge is important for calculation of donor ionization energies, which however changes apparently for Li codoping with Al or Ga in CuO as we have shown previously. In figure 5.10, we show the schematic band diagrams for Li codoping with Al and Ga in CuO at concentration of 4.2%. Since the impurity band below the conduction band is empty, electron at the deep donor level can be excited to this band. Therefore, the excitation energies of single Al and Ga dopants with respect to the

impurity band can be reduced to around 0.2-0.3 eV. If *n*-type complexes can form, their ionization energies should be even lower (~ 0.1 -0.15 eV), helping to increase the electron concentration. It is noted that to reach reasonable electron mobility, the codoping concentration should go beyond a certain value as it has been demonstrated in figure 5.5.

Figure 5.10: Schematic band diagrams for Li codoping with Al (left) and Ga (right) in CuO, as well as the calculated donor levels in the gap.

5.5 Other Donor and Acceptor Combinations

5.5.1 Density of States for $\text{III}_{\text{Cu}}\text{-N}_{\text{O}}$ (III=Al, Ga and In)

We also test other combinations of donor and acceptor, for example, group III elements (Al, Ga and In) codoping with N acceptor. The calculated total DOS of one $\text{III}_{\text{Cu}}\text{-N}_{\text{O}}$ complex (III=Al, Ga and In) in a 96 atom CuO supercell is shown in figure 5.11. From the total DOS, the CBM does not change apparently as compared with pure CuO; however, some occupied impurity states emerges above the VBM of CuO, which could not benefit *n*-type doping by decreasing the donor ionization energy. Similarly as the

$2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ n -type complex that we have discussed in sec. 5.3, the donor-acceptor level repulsion may enhance the donor level slightly, but it is hard to give rise to a very shallow donor level in CuO by Al or Ga codoping with N acceptor due to the deep character of Al and Ga single dopants.

For pure CuO, the VBM is mainly composed of hybridized Cu $3d$ and O $2p$ states. From the partial DOS for Ga-N codoping in figure 5.12, it is shown that the occupied impurity states above the VBM are mainly from N $2p$ state, which has higher orbital energy as compared with that of oxygen. The calculated partial DOS for Al-N and In-N are very similar and therefore are not shown here.

Figure 5.11: The total density of states of $\text{III}_{\text{Cu}}\text{-N}_{\text{O}}$ ($\text{III}=\text{Al}$, Ga and In) in a 96 atom CuO supercell. The Fermi level for pure CuO is set at zero. The black dashed line is the total DOS for pure CuO. The vertical dotted line is the Fermi level of codoped CuO.

Figure 5.12: The partial DOS of $\text{Ga}_{\text{Cu}}\text{-N}_{\text{O}}$ in CuO. The Fermi level for pure CuO is set at zero. The vertical dotted line is the Fermi level of codoped CuO.

5.5.2 Formation Energy of the $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ Complex

The formation energy of Li codoping with Zr is shown in figure 5.13 as a function of the Fermi levels, which is compared with that for Zr single dopant. In the model, both Zr and Li occupy the Cu sites nearest to each other. The calculated binding energy for the $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ complex is -1.44 eV. From figure 5.13, it is found that the formation energy of $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is lower than that of Zr_{Cu} by 0.6 eV and 1.57 eV under O-poor and O-rich conditions, respectively. Therefore, adding a small amount of Li may help to increase the solubility of Zr in CuO. But, the calculated (0/+1) transition energy level of $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ does not change as compared with that for Zr single dopant, because of the weak repulsion between Zr *d* donor state and Li *s* acceptor state. Due to the high formation

energy of Zr single dopant, there is very few probability to form the $n\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ clusters ($n=2,3$) in CuO, which is therefore not calculated here.

Figure 5.13: Formation energy of the $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ complex as a function of Fermi levels, in the O-poor and O-rich conditions, respectively. The formation energy of Zr single dopant is also shown for comparison.

5.6 Summary

In conclusion, we have demonstrated the effect of donor-acceptor (n - p) codoping on reducing donor ionization energies in CuO using first-principles calculations. Our results indicate that N acceptor codoping with both Zr and In can form shallower n -type defect complexes, but their formation energies are very high for practical applications. On the other hand, the solubility of Al/Ga can be improved by codoping with Li acceptor, due to the large binding energies between n -type and p -type dopants. Moreover, Li acceptor codoping with Al/Ga can form shallower n -type complexes ($2\text{Al}_{\text{Cu}}/2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$). It is also observed that Li codoping induces an empty impurity band below the CBM, which can

narrow the band gap and reduce donor ionization energies if the codoping concentration is high enough to reach good electron mobility. Furthermore, we test other donor and acceptor combinations. For example, $2\text{In}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is not a stable complex due to the large atomic size of In. Moreover, N codoping with group III elements (Al, Ga and In) maintains the CBM of CuO but elevates the VBM, which is not beneficial for *n*-type doping. Though the formation energy of $\text{Zr}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is lower than that of Zr_{Cu} , its donor level is not enhanced at all. Our results can be used in the experimental design of suitable *n*-doping strategy for CuO, which is critical for its application in photovoltaic devices.

Chapter VI Experimental Confirmation of (some of) the Predictions

6.1 Introduction

CuO is a well known *p*-type semiconductor due to intrinsic copper vacancies [20-22]. Our theoretical calculations have shown that copper vacancy is easy to form under O-rich condition. However, the reported electrical conductivity is low at about 0.01-0.001 S/cm. To optimize solar cell efficiency and decrease heat loss during operation, it is important to increase the conductivity and control the defect concentration in *p*-type CuO.

On the other hand, it is difficult to fabricate *n*-type CuO. Theoretical calculations suggest that oxygen vacancy is a deep donor, which can not contribute to *n*-type conduction effectively [23]. Recently, Lu *et al.* reported the realization of *n*-type CuO by reactive magnetron sputtering using pure copper target [33]. Although the x-ray diffraction data has shown single CuO phase, the possibility of Cu contamination contributing to the measured electron concentration can not be ruled out. Figueiredo *et al.* also reported *n*-type CuO by thermally oxidizing evaporated metallic Cu films [35]. However, the underlying mechanism is still under debate.

Following our theoretical calculations, we conduct experimental studies on the electrical conductivity of both Li and Zr doped CuO films prepared by pulsed laser deposition. The experimental results are compared with our theoretical predictions, and the cause of discrepancy between theoretical and experimental results is also discussed.

6.2 Experimental Details

In this study, both doped and undoped CuO thin films are prepared using the pulsed laser deposition method on glass substrates. The targets are fabricated using conventional ceramic sintering process. All targets have 1-inch diameter and 1/4-inch thickness. Three CuO: Li targets are sintered from the mixture of CuO powder with 1 wt.% , 4 wt.% , and 8 wt.% Li₂O powder, respectively. One CuO: Zr target is sintered from the mixture of 95 wt.% CuO powder with 5 wt.% ZrO₂ powder. A KrF excimer laser ($\lambda=248$ nm, pulse width=20 ns) is used for the film deposition. The target-substrate distance is kept at 50-60 mm during deposition. Both target and substrates are mounted onto a rotating holder to obtain uniform thin films. The laser energy density and repetition rate are 1 J/cm² and 10 Hz, respectively. The chamber is pumped to a base vacuum of 4×10^{-4} Pa using a turbo molecular pump system.

After deposition, the thickness of the film is measured using Alpha-step surface profiler (KLA Tencor, ASIQ). The crystal structure and orientation of the films are characterized using a Shimadzu XRD-6000 diffractometer with Cu K α radiation at $\lambda=1.5406$ Å. The microstructure and composition of the films are investigated using JSF-7600F field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). The electrical resistivity, carrier concentration and mobility are measured using the four-point probe van de Pauw method. Metal Au is used as electrodes to achieve good contacts. The absorption spectra are obtained using a double beam UV-Vis-NIR spectrophotometer (Agilent Technologies, Cary 5000). The

photoelectrochemical (PEC) characterization is conducted to study the photocurrent in dark and under illumination in a three-electrode configuration.

6.3 *P*-type CuO by Li doping

6.3.1 Optimization of Deposition Parameters for Li dopant

The electrical properties of Li doped CuO films are studied against various oxygen pressure and substrate temperature during the deposition. The thickness of thin films is ~100-200 nm, which can be adjusted by the deposition time. After the deposition, the chamber is filled with oxygen gas and the films are all cooled down in the same oxygen pressure of 10 Torr. Here, we first discuss the effect of growth conditions on the electrical properties of Li doped CuO films.

In pulsed laser deposition, the substrate temperature is crucial for the crystallinity of the resulting film, which is investigated first. As shown in figure 6.1, the resistivity of CuO: Li (1 wt.%) film decreases as the growth temperature increases up to 400 °C. Further increase in deposition temperature leads to increasing resistivity. It was found that CuO film prepared at low temperature has poor crystallinity, which explains the increase in the resistivity when $T_{\text{sub}} < 400$ °C. It is also noted that Li element is easy to evaporate at high temperature, which can affect its doping efficiency significantly. Therefore, the optimized temperature for Li doping is 400 °C in our experiment. By changing the oxygen pressure during the deposition at each substrate temperature, we map out the optimized deposition window for CuO in our system as shown in figure 6.2. The lowest resistivity of CuO: Li (1 wt.%) films is observed at the substrate temperature

of ~ 400 °C and oxygen pressure in the range of 0.1 Pa to 0.4 Pa.

Figure 6.1: Relationship between the substrate temperature and the electrical resistivity of CuO: Li (1 wt.%) films with the oxygen pressure fixed at 0.13 Pa.

Figure 6.2: Resistivity ($\Omega \cdot \text{cm}$) of CuO: Li (1 wt.%) films deposited at different oxygen pressures and substrate temperatures. The optimized temperature is 400 °C and the range of oxygen pressure is 0.1 Pa~0.4 Pa.

Table 6.1: Hall measurement results for CuO: Li (1 wt.%) films prepared at different growth conditions.

<i>Sample</i>	$T_{sub} (^{\circ}C)$	$P_{O_2} (Pa)$	$\rho (\Omega \cdot cm)$	<i>Carrier Type</i>	$\mu (cm^2/Vs)$	$n (cm^{-3})$
S1	500	13	50.2	<i>p</i>	0.25	5×10^{17}
S2	500	1.3	20.4	<i>p</i>	0.37	8.2×10^{17}

To confirm the type of conduction in the film, we conduct hall measurement (Table 6.1) on the samples deposited at 500 °C with the largest resistivity. It shows that CuO: Li (1 wt.%) films prepared at this temperature are *p*-type, consistent with our prediction. Since higher substrate temperature leads to more Li evaporation, those films deposited at lower temperatures should be *p*-type as well. However, the Hall measurement also reveals that the film prepared at a lower oxygen pressure of 1.3 Pa has a slightly higher hole concentration, which contradicts our theoretical prediction of more oxygen vacancies will compensate some of the holes produced by Li doping. This may be related to the amount of Li atom being scattered by the oxygen gas before reaching the substrate, which means low oxygen pressure actually allows more Li to be incorporated in the film. Li deficiency in the thin film prepared by PLD in an oxygen environment is also found in other lithium-containing oxide like LiNbO₃, LiCoO₂, etc [121-123]. A quantitative study has confirmed that light element Li is scattered more than the heavy atoms by the background O₂ molecules, leading to the large loss of Li not reaching to the substrate [124].

Moreover, our calculations predict that Li has an acceptor level of 0.03 eV above the VBM in CuO, which means that the majority of Li dopants can be easily ionized at room temperature. However, the measured carrier concentration for S2 is only around 10^{18} cm^{-3} , which is two orders of magnitude smaller than the nominal concentration of Li in the doping source. Therefore, the loss of Li during the film deposition is significant, especially at high substrate temperature. On the other hand, films deposited at 400 °C show carrier concentrations much closer to the theoretical value.

Figure 6.3: Measured electrical resistivity of pure and Li-doped CuO with different doping concentrations at the optimized growth conditions.

The resistivity of CuO film as a function of Li doping concentration is shown in figure 6.3. Without doping, the resistivity of pure CuO thin film can be as large as 100 $\Omega \cdot \text{cm}$, very high for solar cell application. However, with 1 wt.% Li doping, the resistivity of CuO sample is dramatically reduced to $\sim 2.2 \text{ } \Omega \cdot \text{cm}$. By increasing Li doping concentration to 8 wt.%, the resistivity of CuO sample is further reduced to $\sim 0.35 \text{ } \Omega \cdot \text{cm}$,

which is improved by more than 2 orders of magnitude compared with the resistivity of undoped CuO. Note that the doping concentration refers to the amount of Li in the source target, the actual content in the films are not known. The carrier concentration for 8 wt.% Li doped CuO sample is estimated to be $\sim 10^{20} \text{ cm}^{-3}$. Therefore, by adjusting the deposition parameters and controlling the doping concentration, we can prepare good *p*-type CuO with a wide range of electrical conductivity for solar cell application.

6.3.2 Microstructure and Annealing Effect on CuO: Li Films

We have identified that high substrate temperature can lead to the loss of Li element in the thin film deposition process. However, films prepared at 400 °C have very poor crystallinity, which should affect its application in the solar cell. Post-deposition annealing in O₂ gas (~10 Torr) is used to improve the crystallinity of Li doped CuO films which are annealed at 600 °C for 2 hours on quartz substrate. The thickness of the film is about 400 nm. The crystal structure of the 8 wt.% Li doped CuO films is analyzed using X-ray diffraction as shown in figure 6.4(a). From the X-ray diffraction (XRD) data, the sample shows good crystallinity. All diffraction peaks can be indexed as monoclinic CuO by comparison with the JCPDS card file no. 48-1548 and no characteristic peaks from other copper oxide phases like Cu₂O or the dopant oxide phase Li₂O are found. No obvious peak shift is observed in the XRD as compared with pure CuO. One possible reason is that the actual Li content in the films is much less than that in the target due to the high volatility of Li. In figure 6.4(a), the preferred crystalline orientation of the films are (-111) and (111), which are identified as the most stable facets of CuO thin films in

our experiment. The microstructure of the film is shown in figure 6.4(b). The average grain size of the sample is larger than 100 nm. The measured electrical resistivity of those annealed samples is slightly reduced as compared with the as-deposited one.

Figure 6.4: (a) XRD pattern and (b) SEM image of CuO: Li (8 wt.%) film deposited at 400 °C and 0.4 Pa on quartz substrate and annealed in O₂ gas at 600 °C for 2 hours.

6.3.3 Optical Band Gap of CuO: Li Films

The optical absorption spectrum of 8 wt.% Li doped CuO film is shown in figure 6.5(a). It can be seen that the sample has strong optical absorption in the visible light range (390-700 nm), indicating that CuO is suitable for solar energy harvesting. The optical band gap of CuO thin films can be extracted from the relationship between

absorption coefficient (α) and photon energy (E) for the indirect transition as:

$$(\alpha E)^{1/2} \propto (E - E_g) \quad (6-1)$$

In figure 6.5, the inset figure is the plot of $(\alpha E)^{1/2}$ versus photon energy for determination of the band gap for the sample. The band gap of Li doped CuO is calculated to be around 1.28 eV, which is close to the value for bulk CuO as reported in the literature. Therefore, Li doping does not change the CuO band gap, which is in good agreement with other experimental study [11]. In figure 6.5(b), it shows the calculated density of states for Li doped CuO in a 96 atom supercell. It is clearly that no impurity state is found in the forbidden gap of pure CuO and the change of band gap value can be neglected.

Figure 6.5: (a) UV-Vis-NIR spectrum of Li-doped CuO sample. The inset is the plot of $(\alpha E)^{1/2}$ vs E showing an indirect band gap of 1.28 eV. (b) The calculated density of states for Li doped CuO in a 96 atom supercell.

6.3.4 Summary

In summary, Li doping induces significant changes in the electrical conductivity of CuO films. *P*-type conduction is confirmed by the Hall measurement results. The loss of Li during the deposition process is found to be significant and the doping condition has been optimized by adjusting the substrate temperature and oxygen pressure. It is also shown that the resistivity of CuO films can be as low as $0.35 \Omega \cdot \text{cm}$ for 8 wt.% Li in the doping source.

6.4 Attempt to obtain *n*-type CuO by Zr Doping

In an attempt to obtain *n*-type CuO, we deposit CuO films using a target with 5 wt.% Zr doping. The EDX result of the target is shown in figure 6.6 and the Zr-related peak can be found in the spectrum, which gives the Zr weight percentage around 5%. The O/Cu atomic ratio is slight larger than one. Therefore, the element weight and atomic percentage in the target show good agreement with the nominal one.

Figure 6.6: Energy dispersive X-ray spectroscopy (EDX) for 5 wt.% Zr doped CuO target.

Table 6.2: Measured resistivity of CuO: Zr (5 wt.%) thin films prepared under different conditions.

Sample ID	P _{O2} (Pa)	T _{sub} (°C)	ρ ($\Omega \cdot \text{cm}$)
Zr1	13	500	45.2
Zr2	13	600	21.4
Zr3	1.3	500	62.4

Our theoretical calculations have indicated that oxygen poor growth condition should be adopted for *n*-type doing to limit the formation of copper vacancy. To optimize the deposition conditions for Zr doping, three Zr doped CuO films are prepared under different oxygen pressure and temperature, which are listed in Table 6.2. The thickness of the films is ~200 nm. After the deposition, the films are cooled down in high oxygen gas pressure to obtain pure CuO phase as it is indicated from the XRD data. No mixed phase of ZrO₂ and CuO was found from XRD data.

Unfortunately, these films all show high resistivity and it is not possible to conduct Hall measurement to determine the conduction type. Instead, we construct a three-electrode electrochemical cell and measure the photocurrent density under a 90 W white lamp. The mechanism of PEC measurement and the photocurrent result are shown in figure 6.7(a) and 6.7(b), respectively. The applied voltage is 0 V vs an Ag/AgCl/saturated NaCl reference electrode. Platinum is the counter electrode. The solution contains 0.5 M Na₂SO₄. The CuO: Zr sample is deposited on FIO substrate at 500 °C and 1.3 Pa. The cathodic current when light is shining on the sample (working electrode) indicates that the CuO: Zr film is a *p*-type semiconductor. The measured

photocurrent density for undoped CuO is however very similar.

Figure 6.7: (a) Mechanism of the production of photocurrent in an electrolyte solution by a *p*-type photocathode. (b) Photocurrent measured for the Zr-doped CuO film using a standard three-electrode photocurrent cell.

Despite that our calculations show Zr should be an *n*-type dopant for CuO, the measured *p*-type conduction indicates that the majority carrier is hole. Thus, intrinsic copper vacancy is expected to be the dominate defect in these films, which is relatively easy to form due to the volatility of copper atom. We conduct the energy dispersive X-ray (EDX) measurement of the ratio of elements in the CuO: Zr films. In the EDX results of

all Zr doped CuO films (see figure 6.8 for Zr3), no Zr-related peak is observed in the spectrum, indicating that Zr is not successfully doped into CuO. Other peaks in the spectrum should come from the substrate. This result agrees with our theoretical prediction that Zr dopant has low solubility in CuO due to its large atomic size.

Figure 6.8: Energy dispersive X-ray spectroscopy (EDX) for CuO: Zr thin films (Zr3).

6.5 Summary

Experimental studies on both Li and Zr doped CuO thin films prepared by pulsed laser deposition using Li_2O and ZrO_2 as the dopant sources are conducted. The *p*-type conduction is shown to be improved by using Li dopant, which agrees well with our theoretical predictions. The effect of substrate temperature and oxygen pressure on the Li doping efficiency is optimized. Post-deposition annealing on quartz substrate could improve the crystallinity of thin film and further decrease the resistivity. However, *n*-type conduction is not achieved by using Zr dopant, and the Zr element is not detected in the EDX analysis. Our theoretical results can explain that Zr dopant has a low solubility in CuO and *n*-type doping is very challenging because of copper vacancy.

Chapter VII Conclusions and Future Work

7.1 Conclusions

We have conducted a systematic analysis on the intrinsic defects and potential dopants for CuO using first-principle DFT calculations. The intrinsic defects determine the properties of the as-prepared CuO. However, extrinsic dopants are needed to better control the electrical properties of CuO for practical applications. We have selected the potential *p*-type (group IA elements) and *n*-type dopants (group IIIA and IVB elements) by comparing the ionic size and valence states with those of Cu in CuO. After investigating the formation energies and ionization levels of the potential dopants, we further study the donor-acceptor codoping effect on the donor level in CuO. Finally, preliminary experiments have been conducted to verify our theoretical predications on two different doping systems.

Here we summarize the main conclusions of this thesis, which we hope to evoke more theoretical and experimental investigations on this interesting and potentially useful material.

- (1) For intrinsic defects, we find that copper vacancy is a shallow acceptor and the dominant defect type under oxygen rich condition, which explains the origin of *p*-type conduction in as-prepared CuO. On the other hand, oxygen vacancy is a very deep donor, which can hardly make CuO *n*-type. However, it can act as hole killer under oxygen poor condition.

- (2) For extrinsic dopants, our calculations indicate that Li and Na are shallow acceptors whose formation energies are even lower than that of copper vacancy under both oxygen rich and oxygen poor conditions. They can help to produce robust *p*-type CuO. However, it is also found that *n*-type conduction is much more difficult to achieve in CuO. First, Al, Ga and Ti dopants have deep donor levels in the band gap and can not contribute electrons to the conduction band at room temperature. Secondly, In, Zr and Hf dopants have relatively shallow donor levels of around 0.2-0.3 eV (still quite deep for practical use), but the dopant solubility in CuO is quite low due to their large ionic sizes as compared with Cu^{2+} . It is also observed that less electronegative elements tend to produce shallower donor levels.
- (3) For codoping, it is found that N codoping with both Zr and In can form shallower *n*-type defect complexes which are thermodynamically stable in CuO. But it is very hard to be realized in experiments, because it is challenging to incorporate N atoms into the O site. On the other hand, Li codoping with Al/Ga are predicted to form defect complexes easily due to the large binding energies and low formation energies. Furthermore, it can modify the electronic structure of CuO by producing an empty impurity band below the host CBM. At high codoping concentrations, *n*-type CuO can be achieved by tuning the ratio of Li acceptor and Al/Ga donor.
- (4) Our experimental study has confirmed that Li doping in CuO can improve the *p*-type conductivity. After optimizing the deposition parameters, the resistivity of Li doped CuO films can be as low as 0.35 $\Omega\cdot\text{cm}$, which is about 3 orders of magnitude lower

than that for undoped CuO films, agrees well with our theoretical predictions. However, Zr doping is very ineffective and the resistivity of Zr doped CuO does not change apparently as compared with undoped one. Electrochemical photocurrent measurement shows that Zr doped CuO films should be *p*-type, likely due to the dominating intrinsic defect: copper vacancy. Therefore, the low solubility of Zr dopant in CuO limits its doping efficiency.

7.2 Future Work

Although our preliminary experiments have confirmed some of the theoretical predictions, further investigations are needed in the following directions:

- (1) The carrier concentrations of Li doped CuO films are much smaller than expected values based on the Li content in the target. What is causing this discrepancy needs to be clarified. There are two possible reasons: (i) the actual Li content in the film is less than that in the target due to the high volatility of Li; or (ii) intrinsic defects exist in the films that compensate the Li dopants. Further analysis on the composition of the films may shed light on this issue.
- (2) We have shown in the preliminary experiment that Zr doping in CuO is challenging, consistent with the theoretical prediction. It is unlikely that *n*-type CuO can be achieved by single doping. However, our calculations also show that donor-acceptor codoping could increase the dopant solubility and reduce the donor ionization level significantly. Currently, there is no experimental work regarding the donor-acceptor codoping in CuO. We thus suggest trying Li and Al/Ga codoping to achieve *n*-type CuO.

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