**pH-dependence of conduction type in cuprous oxide synthesized from solution**

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(Received 27 April 2010; accepted 18 May 2010; published online 28 June 2010)

The formation of native point defects in cuprous oxide, Cu2O, synthesized from solution has been studied by first-principles calculations. Although p-type conduction is obtained in Cu2O synthesized from vacuum regardless of copper-rich or oxygen-rich conditions, intrinsically n-type Cu2O without doping can be grown in a strong acidic environment from solution. Our calculations show that both n-type and p-type Cu2O can be obtained depending on the solution pH value, which are in good agreement with our experimental results. © 2010 American Institute of Physics. [doi:10.1063/1.3452383]

I. INTRODUCTION

Cuprous oxide (Cu2O) has been regarded as one of the promising solar-cell materials1,2 due to the low cost associated with its solution syntheses, along with its nontoxicity and the natural abundance of its source materials. It has been known as a naturally p-type semiconductor for a long time.3–8 The p-type nature has been explained by first-principles studies under either copper-rich or oxygen-rich conditions recently.9–11 which is ascribed to native point defects, similar to those in cupric oxide (CuO).12 However, under specific circumstances, n-type Cu2O has been deposited electrochemically without any external dopant.13,14 We reported both n-type and p-type Cu2O and its p-n homojunctions by electrochemical deposition recently.14 Capacitance-voltage (C-V) measurements clearly demonstrated n-type or p-type conduction characters depending on the pH value of the deposition solution.

The present work focuses on first-principles calculations on native point defects in Cu2O synthesized under solution environments. The objective of the study is to achieve a fundamental understanding on the mechanism controlling the conduction type in Cu2O under different solution conditions. The formation energies of various native point defects in Cu2O are calculated. They include vacancies (V Cu or V O, where the subscript refers to the missing host atom), antisite defects (CuO or O Cu where A B means “B” atom site is occupied by “A” atom), and isolated interstitials (O, or Cu) both in vacuum-based and solution-based growth environments. In the solution environment, our results show that both n-type and p-type Cu2O can be obtained by controlling the solution pH value, which agrees well with our experimental measurements.

II. COMPUTATIONAL METHOD AND RESULTS

All the present calculations were performed using the VASP package15–19 based on the Kohn–Sham formulism of density-functional theory (DFT). The local density approximation for the exchange correlation functional proposed by Perdew and Zunger was adopted.20 In order to reduce the number of plane wave basis functions necessary for accurately describing the electronic wave functions, the projector augmented wave (PAW) method21,22 implemented in VASP (Ref. 19) was used to describe the electron-ion interactions. The PAW potential for Cu was generated from the atomic configuration of [Ar]3d104s1. The 3d and 4s electrons were treated as valence electrons. For O, the atomic configuration to generate the PAW potential was [He]2s22p4 and the 2s and 2p electrons were considered as valence electrons. The plane-wave energy cutoff was set at 400.0 eV to ensure the convergence of the calculations.

The Cu2O crystal has a simple cubic unit cell with two molecules in it. Each of the two oxygen atoms, one at the corner and another at the body center, is surrounded by a tetrahedron of copper atoms. Each copper atom is two-coordinated with two oxygen atoms. In calculations of native point defects in Cu2O, to avoid the artificial interaction of neighboring defects due to the periodic boundary conditions, we adopted a supercell as large as 2 × 2 × 2 unit cell, which contains 48 atoms in a perfect crystal structure. In the calculations, the integrations over the first Brillouin zone were made by using a 4 × 4 × 4 k-point set generated according to the Gamma-centered Monkhorst–Pack scheme23 for the supercell. The optimized crystal lattice constant is 4.20 Å, which is in good agreement with the experimental value 4.27 Å.24

We considered three different types of native point defects: vacancies (V Cu or V O), antisite defects (CuO or O Cu), and isolated interstitials (O or Cu). A vacancy was introduced by removing a Cu atom or O atom from its site in the supercell. For the antisite defects, an O atom was replaced by a Cu atom or a Cu atom was substituted by an O atom in the supercell. In the case of isolated interstitials, an atom of Cu or O was put into possible high-symmetry interstitial sites in the supercell. After a defect was introduced, all the atoms were allowed to relax according to the Hellmann–Feynman forces until the change in the total energy was less than 0.001 eV/cell.
The formation energy, $E_f$, for a defect with charge $q$ (including its sign, $q$ is the number of electrons transferred from the defect to the reservoirs) in Cu$_2$O can be expressed as a function of Fermi level of electrons ($\varepsilon_F$) as well as atomic chemical potentials

$$E_f = E_f(\text{defect;}q) - E_f(\text{perfect}) + qE_{\text{VBM}} - n_{\text{Cu}}\mu_{\text{Cu}}$$

$$- n_{\text{O}}\mu_{\text{O}} + q\varepsilon_F,$$  

(1)

where $E_f(\text{defect;}q)$ and $E_f(\text{perfect})$ are the total energies of a supercell with and without the defect, respectively, $n_{\text{Cu}}$ ($n_{\text{O}}$) denotes the number of Cu (O) atoms removed from or added into the perfect supercell (e.g., $n_{\text{Cu}}=+1$ and $n_{\text{O}}=0$ for Cu vacancy; $n_{\text{Cu}}=-1$ and $n_{\text{O}}=0$ for Cu interstitial), and $\mu_{\text{Cu}}$ ($\mu_{\text{O}}$) is the corresponding chemical potential. $E_{\text{VBM}}$ is the energy of the valence band maximum (VBM) of the perfect system and $\varepsilon_F$ is the Fermi level of electrons referenced to the VBM, which can be considered as the chemical potential for electrons. By adding the term $qE_{\text{VBM}}$, the zero point of the single electron energy level is shifted to a well-defined position, i.e., VBM.

**A. Native defects formation energies in a vacuum-based growth environment**

The chemical potentials depend on the growth conditions, which can be Cu rich or O rich in a vacuum-based environment, and anything in between. Under Cu-rich conditions, Cu is assumed to be in a thermodynamic equilibrium with bulk Cu and, therefore, $\mu_{\text{Cu}}=\mu_{\text{Cu}}[\text{bulk}]$, where $\mu_{\text{Cu}}[\text{bulk}]$ is the total free-energy per atom of bulk Cu. The O chemical potential in this case is not independent but constrained by the equilibrium condition

$$\mu_{\text{O}} + 2\mu_{\text{Cu}} = \mu_{\text{Cu}_2\text{O}},$$  

(2)

where $\mu_{\text{Cu}_2\text{O}}$ is the chemical potential of the perfect Cu$_2$O crystal. Under O-rich conditions in the vacuum-based growth environment, O is assumed to be in equilibrium with O$_2$ gas, so its chemical potential is $\mu_{\text{O}}[\text{gas}]$, the total energy per atom of a molecular O$_2$. In this case, $\mu_{\text{Cu}}$ is determined by Eq. (2). To obtain $\mu_{\text{Cu}}[\text{bulk}]$ and $\mu_{\text{O}}[\text{gas}]$, separate calculations were performed to get the total energies of metallic Cu and molecular O$_2$.

The formation energies of various native point defects in Cu$_2$O as a function of the Fermi level $\varepsilon_F$, which varies from VBM to the conduction band minimum (CBM), are shown in Fig. 1. Only the lowest-energy charge states at a given $\varepsilon_F$ are shown. Under the Cu-rich condition, copper vacancy has the minimum formation energy which indicates its p-type character. The negative slope for VCu indicates that the Cu vacancy prefers to capture electrons. Therefore, copper vacancy acts as an acceptor in Cu$_2$O. For atomic relaxation around Cu vacancy, the two nearest O atoms are displaced inward by 5.17% of the equilibrium Cu–O bond length. For interstitial defects, the equilibrium geometries in Cu$_2$O are those of tetrahedral (T$_d$) and octahedral interstitial sites. Among them, the total energy in T$_d$ sites is the lowest. The formation energies of the interstitials are significantly higher than that of copper vacancy, suggesting a less important role for the interstitials. The formation energy of antisite defect O$_{\text{Cu}}$ is also higher than that of copper vacancy. For oxygen vacancy, $V_{\text{O}}$, the present calculation shows that it prefers to be in its neutral charge state. For the atomic relaxation around O vacancy, the four nearest Cu neighbors are displaced inward by 17.9% of the equilibrium Cu–O bond length.

Under the O-rich condition, $V_{\text{Cu}}$ has the lowest formation energy as well, and its value is slightly smaller than that under the Cu-rich condition. The formation energies of $V_{\text{O}}$, $O_{\text{Cu}}$, and $V_{\text{Cu}}$ decrease as compared to those under the Cu-rich condition. On the other hand, the formation energies of $V_{\text{O}}$, $O_{\text{Cu}}$, and $O_{\text{Cu}}$ increase as compared to the corresponding values under the Cu-rich condition. At the two extreme conditions, Cu-rich or O-rich, we found that $V_{\text{Cu}}$ has always the lowest formation energy, indicating that there is spontaneous formation of Cu vacancy during the growth of crystalline Cu$_2$O in the vacuum-based environment, leading to an intrinsic p-type material. These results agree well with experimental results$^{25-28}$ and previous theoretical studies.$^{9-11}$

**B. Amphoteric conduction mechanism in a solution-based growth environment**

Although p-type Cu$_2$O is unavoidable in a vacuum-based growth environment, our recent electrochemical deposition experiments$^{14}$ showed that n-type Cu$_2$O was grown without doping by controlling the pH value in a copper sulfate solution. In the experiments, Cu$_2$O was electrochemically deposited from a solution containing 0.4 M copper(II) sulfate and 3 M lactic acid. The pH value of the solution was varied between 6.5 to 12.0 by addition of 4 M sodium hydroxide. In the solution, copper(II) (Cu$^{2+}$) ions are reduced to copper(I) (Cu$^{+}$) ions, which is followed by a hydrolysis reaction,

$$2\text{Cu}^2+ + 2\text{OH}^- = \text{Cu}_2\text{O}_4^- + \text{H}_2\text{O}.$$  

(3)

In an electrolyte solution, copper exists in an ionic form which is hard to exactly determine its chemical potential. On the other hand, the OH$^-$ concentration can be represented by the solution pH value. An OH$^-$-rich condition corresponds to a high OH$^-$ concentration, i.e., a high pH value. At the extremely basic limit, OH$^-$ has its highest chemical potential

![FIG. 1. Formation energies as a function of Fermi level for native point defects in Cu$_2$O under (a) O-rich and (b) Cu-rich conditions in vacuum-based growth. The zero point of the Fermi level corresponds to the top of the valence band. Only segments corresponding to the lowest-energy charge states are shown. The slope of these segments indicates the charge. Kinks in the curves indicate transitions between different charge states.](image-url)
since OH\textsuperscript{−} exists in the solution with the maximum activity as compared to the minimum activity in the extremely acidic environment. At the acidic limit, OH\textsuperscript{−} is combined easily with H\textsuperscript{+} to form a relatively stable H\textsubscript{2}O molecule, resulting in a lower chemical potential for OH\textsuperscript{−}. To simplify the problem, we just consider OH instead of OH\textsuperscript{−} in our following discussions. To find the chemical potential of OH, \(\mu_{\text{OH}}\), a total energy calculation was performed on isolated OH. The chemical potential of OH in a solution at the extremely basic limit was approximated as the same as that of isolated OH. The total energy of OH, i.e., \(\mu_{\text{OH}}\), was found to be \(-7.81\) eV. This was regarded as the upper bound. On the other hand, the lower bound of OH chemical potential is constrained by H\textsubscript{2}O, which is \(-2.85\) eV in good agreement to the experimental value of \(-2.50\) eV for H\textsubscript{2}O. Copper atomic chemical potential can then be determined by the thermodynamic equilibrium of Eq. (3),

\[
\mu_{\text{Cu}} + \mu_{\text{OH}} = (\mu_{\text{Cu}_2\text{O}} + \mu_{\text{H}_2\text{O}})/2 ,
\]

where \(\mu_{\text{H}_2\text{O}}\) is the chemical potential of water molecule, which is \(-14.84\) eV in the present calculations. As a test, the present calculations obtained a formation enthalpy of \(-3.00\) eV for H\textsubscript{2}O, in good agreement to the experimental value of \(-2.85\) eV. Copper atomic chemical potential can then be determined by the thermodynamic equilibrium of Eq. (3),

\[
\mu_{\text{Cu}} + \mu_{\text{OH}} = (\mu_{\text{Cu}_2\text{O}} + \mu_{\text{H}_2\text{O}})/2 ,
\]

since the right-hand side is a constant, \(-15.41\) eV from the present calculations. In the OH\textsuperscript{−}-rich case, i.e., the extremely basic limit, the chemical potential of a copper atom, \(\mu_{\text{Cu}_2\text{O}}\), was found to be \(-7.60\) eV from Eq. (4), where \(\mu_{\text{OH}}\) is taken as the same as that of isolated OH. In the present work, the solution environment was simulated from extremely high pH values to extremely low pH values. The \(\mu_{\text{OH}}\) then ranges from \(-7.81\) to \(-14.84\) eV. The latter corresponds to the water chemical potential limit by Eq. (4). This results in the chemical potential of copper, \(\mu_{\text{Cu}_2\text{O}}\), ranging from \(-7.60\) to \(-0.57\) eV. \(\mu_{\text{OH}}\) was assumed to linearly change with the solution pH value. \(\mu_{\text{Cu}_2\text{O}}\) corresponding to a specific pH value can thus be linearly interpolated. At the extremely basic limit, a pH value of 14 corresponds to a \(\mu_{\text{Cu}_2\text{O}}\) of \(-7.60\) eV, while \(\mu_{\text{Cu}_2\text{O}}\) increases to \(-0.57\) eV at the extremely acidic environment with a pH value of 1.

The formation energies of native point defects corresponding to three different solution environments are presented in Fig. 2. They show a change in conduction mechanism of Cu\textsubscript{2}O in solution environment with the pH value changing. Meanwhile in Fig. 3, the experimental results of C-V measurements at three different solution environments are presented. According to Mott–Schottky theory, a negative slope indicates p-type conduction while a positive slope reveals n-type conduction. Figure 2(a) shows defect formation energies in Cu\textsubscript{2}O at pH value of 10, with the chemical potential of Cu at its bulk value, \(-5.44\) eV. Copper vacancy, \(\text{V}_{\text{Cu}}\), acting as an acceptor (−1 charge state), is the dominant defect. It is in good agreement to the experimental measurement shown in Fig. 3(a).

In Fig. 2(b), the pH value is lowered to about 4 with \(\mu_{\text{Cu}_2\text{O}}\) increased to \(-2.20\) eV. The formation energies of three acceptorlike defects, \(\text{V}_{\text{Cu}}\), interstitial oxygen, \(\text{O}_i\) and antisite \(\text{O}_{\text{Cu}}\), rise. On the other hand, the formation energies of \(\text{V}_{\text{Cu}}\), \(\text{Cu}_i\), and \(\text{CuO}\) decreases. The lowest one is \(\text{V}_{\text{O}}\) in the neutral state which provides no carriers. The lowest charge state is either \(\text{Cu}^+_i\) when the Fermi level is near VBM or \(\text{V}_{\text{Cu}}^{-}\) when the Fermi level is close to CBM, exhibiting an amphoteric behavior at that pH value. This corresponds to the experimental case at pH 8 shown in Fig. 3(b).

When the pH value is reduced further down to 2 in the calculation, \(\mu_{\text{Cu}_2\text{O}}\) increases to \(-1.12\) eV. The results are shown in Fig. 2(c). The formation of two donor defects (\(\text{Cu}^\text{+}
\)

![FIG. 2. Formation energies of native point defects in the solution growth environment from a strong base to a strong acid condition. The slope of these segments indicates the charge state. Panels (a), (b), and (c) show a change in the dominant defect, from acceptors (\(\text{V}_{\text{Cu}}, \text{O}_i\), and \(\text{O}_{\text{Cu}}\)) to donors (\(\text{V}_{\text{Cu}}, \text{Cu}_i\), and \(\text{CuO}\)) as the chemical potential of copper atom increases, i.e., the solution becomes more acidic.]

![FIG. 3. Mott–Schottky plots of Cu\textsubscript{2}O deposited electrochemically at decreasing pH values, i.e., (a) 10.0, (b) 8.0, and (c) 6.8. The negative slope in (a) indicates p-type, and the positive slope in (c) suggests n-type. Both positive and negative slopes are observed in (b), revealing amphoteric conduction.]
Materials Sciences and Engineering under Award No. DE-SC0002062. The computational work was done at the High Performance Computing Center of the University of Texas at Arlington. Some of us (W.W. and Q.Z) benefited from discussions with Su-huai Wei and C. G. Van de Walle.

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