Ab initio calculation and electrochemical verification of a passivated surface on copper with defects in 0.1 M NaOH

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A B S T R A C T

The thermodynamic character and dynamic behavior of vacancies in a passivated copper surface were investigated by calculations and experiments, and the data were interpreted in terms of the Point Defect Model (PDM). Both the experimental and computational results show that the principal vacancy in the passive film on copper formed anodically in 0.1 M NaOH solution is the copper vacancy and the diffusion coefficient of the copper vacancy is of the order of 10^{-17} cm^2/s.

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1. Introduction

Copper is used extensively in many industrial applications, because of its superior electronic and thermal conductivity and good corrosion resistance. The good corrosion resistance of copper is due to the formation of a thin passive oxide film on the surface, which inhibits further corrosion. The passive film that forms on copper in alkaline solutions comprising a bilayer structure of Cu_2O as the barrier layer adjacent to the metal and an outer layer of precipitated $Cu(OH)_2$ have been studied qualitatively and quantitatively [1,2]. In addition, Macdonald [3–5] investigated the basic characteristics and mechanisms of semiconductor passive films and proposed the Point Defect Model (PDM). Herbert [6] found that the collective behavior of point defects formed on the free surfaces of ionic crystals under redox conditions can lead to initiation of local breakdown by pitting and the PDM postulates that it is the condensation of cation vacancies at the metal/barrier layer interface that is responsible for passivity breakdown [3–5].

By studying the surface stabilities and photocatalytic properties of Cu_2O microcrystals, Zheng [7] and Xu et al. [8,9] found that the Cu_2O (111) facet can be more stable than other facets. A variety of ab initio calculations using density functional theory (DFT) have been performed to study the adsorption of H_2, CO_x and NO on non-point defective and point-defective Cu_2O (111) surfaces [10–12]. However, simultaneous experimental studies and computational simulations that were designed to investigate the characteristics of the point defects on Cu_2O (111) surfaces are limited.

In this paper, we address the following issues: (a) determination of the semiconductor characteristics of the passive film on a copper surface via experiment and (b) definition of the thermodynamic characteristics and dynamic behavior of the defective Cu_2O (111) surface using ab initio calculation in support of the experimental data.

2. Methods and material

2.1. Experiments

The electrochemical measurements were performed in a conventional three-electrode cell at ambient temperature (22 ± 2 °C), using a working electrode (WE) made from pure copper rod (99.99%, Shang-Hai Hegang). A saturated calomel electrode (SCE) and a Pt plate were employed as reference electrode (RE) and counter electrode (CE), respectively. The working electrode was mounted in epoxy resin with a 1 cm^2 area exposed to the 0.1 M sodium hydroxide solution.

Before potentiodynamic polarization (PDP), a 30 min rest at the open circuit potential (OCP) was allowed, and then PDP was commenced in the negative to positive direction at a scan rate of 0.1667 mV/s. However, prior to PDP, the specimen was cathodically polarized at a potential of -0.6 V$_{SCE}$ for 180 s, to remove air-formed oxidation products. Anodic polarization at various passive film formation

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potentials was performed for 1 h, in order to generate a steady-state passive film. Then, Mott–Schottky experiments were performed by measuring the frequency response at 1 kHz during a 50 mV/s potential scan from −400 to 800 mV$_{SCE}$. Finally, EIS measurements were performed. The frequency was scanned between 0.01 Hz and 100 kHz. All experiments were performed using a PARSTAT 2273 Electrochemical System.

2.2. Computational details

All calculations were performed using the Perdew–Burke–Ernzerhof (PBE) form of the GGA functional with spin polarization based on the DFT method in the VASP 5.3 in MedeA.

The cutoff energy of the plane wave was setup to 520 eV for bulk and 450 eV for slab configurations, and the k-point meshes of $6 \times 6 \times 6$ for bulk and $2 \times 2 \times 1$ for surface were adopted [13]. With these conditions, we obtained a cell parameter of a = 4.31 Å for the bulk Cu_2O, which is overestimated by only 1% with respect to the experimental value [14].

A 5-layer (2×2) unit cell with a 15 Å vacuum region was constructed for modeling the O-terminated Cu_2O (111) surface [13]. There are four types of ions on the Cu_2O (111) surface (Fig. 1) and four types of vacancies on the surface, $V_{Cu_{CSA}}$, $V_{Cu_{CUS}}$, $V_{O_{CSA}}$ and $V_{O_{CUS}}$. To estimate the vacancy formation energies, vacancies were created individually by removing the Cu_{CSA}, Cu_{CUS}, O_{CSA} and O_{CUS} ions in the first layer of the Cu_2O (111) surface, followed by calculating the surface relaxation energies.

To investigate the diffusion behavior of vacancies in the Cu_2O membrane, we used a large model with 120 atoms and created a $V_{Cu_{CUS}}$ that is most likely to occur in Cu_2O in 3rd layer, and then a molecular dynamics calculation was performed. First, starting from the minimized structure, the surface is thermalized at 298 K (NVT ensemble: time step = 1.0 fs) using a Nose thermostat, an external degree of freedom constituting a heat-bath. Thermalization continued until the potential energy was
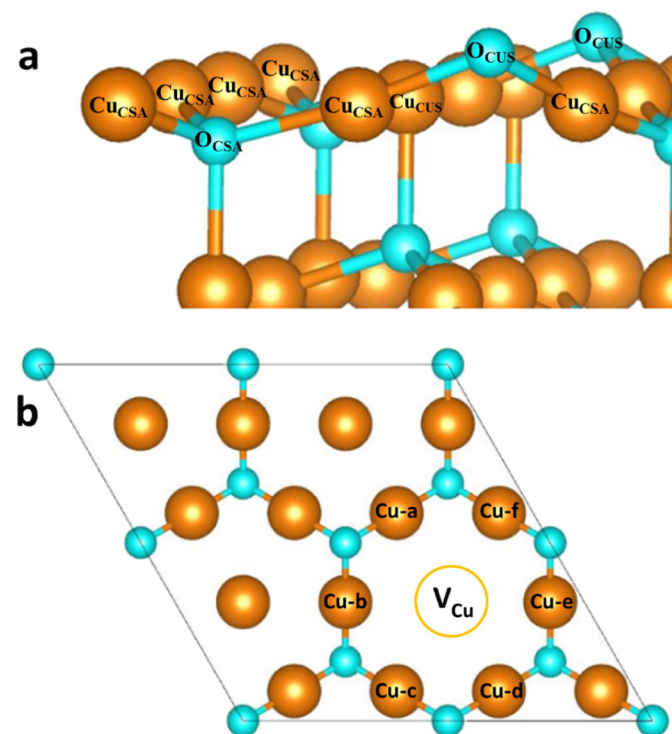

Fig. 1. (a) Side view of the Cu_2O (111) perfect surface; and (b) top view of the Cu_2O (111) surface with the Cu_{CUS} vacancies.

moving within a span of 1.5 eV for a time of 0.3 ps. Next the system was stabilized in a constant pressure and temperature simulation for 1 ps (NPT ensemble: time step = 1.0 fs, initial temperature = 298 K, and external pressure = 101 kPa).

3. Experimental results

Fig. 2(a) shows the potentiodynamic polarization anodic curve of copper in a 0.1 M NaOH solution. It is found that the copper electrode has a wide passive range in this solution. In this paper, we chose 0, 0.1, 0.2, and 0.3 V$_{SCE}$ from the passive range of 0–0.4 V$_{SCE}$ to perform the impedance and Mott–Schottky analyses.

Fig. 2(d) shows the Mott–Schottky plots for the passive films formed on copper at the different formation potentials. As seen, the passive film exhibited p-type semiconducting behavior. Based on the Point Defect Model (PDM) [3–5], cation vacancies are electron acceptors, thereby doping the barrier layer in a p-type manner, whereas oxygen vacancies and metal interstitials are electron donors, resulting in n-type doping. Therefore, the dominant point defect in the passive film on the copper surface is the cation vacancy.

According to Mott–Schottky theory, the space charge capacitance of a p-type semiconductor, as represented by Eq. (1), assuming that the capacitance of the Helmholtz layer is much larger than the space charge capacitance and hence can be neglected [15–22], noting that the capacitances are connected in series:

$$\frac{1}{C^2} = \frac{2}{-\varepsilon\varepsilon_0 eN_A}\left(E - E_{fb} - \frac{kT}{e}\right) \tag{1}$$

yields the electronic character of the film and the acceptor concentration. In this equation, e is the electron charge and N_A represents the acceptor density (cm^{-3}), which can be determined from the slope of the Mott–Schottky plot. The parameter ε is the dielectric constant of the passive film (usually assumed to be 18 for the Cu_2O barrier layer on copper [23]), ε_0 denotes the vacuum permittivity; k, T, and E_{fb} are the Boltzmann constant, absolute temperature, and flat band potential, respectively.

The equation that describes the dependency of the acceptor densities N_A on the formation potential E_{ff} is Eq. (2), where ω_1 and ω_2 are unknown constants [24]. Fig. 2(e) displays the relationship.

$$N_A = \omega_1 \exp(-bE_{ff}) + \omega_2 \tag{2}$$

The diffusion coefficient can then be calculated from Eq. (3) as:

$$D = \frac{i_{ss}RT}{4eF\omega_2\varepsilon_L} \tag{3}$$

where i_{ss} is the steady-state passive current density (Table 1); R and F represent the ideal gas constant (8.314 J/Kmol) and the Faraday constant [96,487 C/mol(e)], respectively; ω_2 has been obtained from Fig. 2(e) (5.09 × 10^{20} cm^{-3}); and ε_L stands for the electric field strength of the barrier layer, which can be obtained from Eq. (4).

$$L_{ss} = \frac{1}{\varepsilon_L}(1-\alpha)E_{ff} + B \tag{4}$$

where α is the polarizability of the barrier layer/solution (bl/s) interface with $0 < \alpha < 1$. A value of $\alpha = 0.5$ was used here, and B is a constant that depends upon the pH [4]. Moreover, the steady-state film thickness L_{ss} can be obtained from Eq. (5) [25].

$$L_{ss} = \frac{\varepsilon\varepsilon_0}{C} \tag{5}$$

where all symbols are defined above. The capacitance C in Eq. (5) was obtained by the equivalent circuit analysis of the EIS [Fig. 2(b)–(c)]. Based on Eqs. (4) and (5), the relationship between the steady-state