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Electrochemical measurements and atomistic simulations of Cl^--induced passivity breakdown on a Cu_2O film

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ABSTRACT

The mechanism of passivity breakdown on Cu_2O films was studied. The thickness and components of the film were estimated by EIS, AES and XPS analyses. The structural relaxations, energies, electronic properties and diffusion coefficients were calculated by first-principles calculations. Both the experimental and calculated results demonstrate that the film thinning is due to the adsorption of Cl^- on the surface instead of a penetration process. The inner point defects facilitate the adsorption of Cl^-, and the introduction of Cl^-, in turn, increases the transport rate of point defects. A theoretical model was proposed, which is also applicable to local breakdown.

1. Introduction

Copper, as a crucial material, has a wide range of applications because of its good mechanical properties and corrosion resistance. The barrier layer of passive film grown on copper surfaces, the Cu_2O film, is responsible for the corrosion resistance [1]. The structure of anodic oxide films has been examined [2–5]. A crystalline and epitaxial Cu(I) oxide layer has been evidenced by in situ electrochemical atomic force microscopy (AFM) [2] and scanning tunneling microscopy (STM) [3–5]. In 0.1 M NaOH, Cu_2O (111) and Cu_2O (001) are formed on Cu (111) and Cu (001), respectively. The Cu_2O (111) oxide film grows on Cu (111) with a faceted surface characterized by a hexagonal lattice in parallel or antiparallel epitaxy on the substrate (Cu_2O (111) [1–10] || Cu (111) [−110] or [1–10]). Herbert [6] illustrated that the collective behavior of point defects formed on the free surfaces of ionic crystals under redox conditions can lead to the initiation of local breakdown by pitting. Macdonald [7–9] proposed the point defect model (PDM) to investigate the properties of passive films and postulated that it is the condensation of cation vacancies at the metal/barrier layer interface that is responsible for passivity breakdown. The barrier layer of copper, the Cu_2O film, is a p-type semiconductor based on the PDM [7–9]. The vacancies of Cu^+ (V'_{Cu}) species are the main carriers that determine the stability and corrosion resistance of the passive film grown on Copper.

Copper undergoes serious corrosion damage in certain highly aggressive environments [10–12]. Cl^- is a naturally and unavoidably corrosive ion in the marine environment. The corrosion behavior of copper in a Cl^--containing medium has been investigated by numerous studies under outdoor and indoor conditions [13–17]. The breakdown of the passive film is caused by the interaction between Cl^- and the Cu_2O passive film that produces chlorides, such as slightly soluble CuCl or soluble $CuCl_2^-$ ($Cu_2O + 4Cl^- + 2H^+ \rightarrow 2CuCl_2^- + H_2O$) [18,19]. $CuCl_2^-$ is considered to be the main cuprous complex in solutions containing Cl^- with a concentration of approximately 0.55 mol L^{-1}, which is roughly equivalent to that of seawater ($[Cl^-]$ = 0.5–0.6 mol L^{-1}). The dissolution of the passive film is dominated by the movement of the chlorides away from the surface into the bulk solution [20]. Although the corrosion mechanism of copper in a medium containing Cl^- is well established, a detailed understanding regarding the interaction between Cl^- and Cu_2O, especially at the atomic scale, remains a key issue. The aim of this study is mainly to focus on two topics regarding the breakdown of the passive film on copper at the atomic scale:

(1) The form of the interaction between Cl^- and the Cu_2O passive film, adsorption or permeation, leading to the breakdown of the passive film, which is from a thermodynamics point of view.
(2) The effect of Cl^- adsorption and incorporation on the transport properties of the passive film, which can be used to evaluate the dynamic stability of the passive film.

For the first topic, there have been no related reports concerning the reaction process between Cl^- and the Cu_2O layer at the atomic scale from the perspective of thermodynamic energies, while the interaction between Cl^- and the passive film of nickel has been systematically

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investigated. The work by the research group of P. Marcus [21–24] evaluated the adsorption and insertion of Cl^- on the hydroxylated NiO surface using density functional theory (DFT) periodic calculations, which revealed the form of reaction between Cl^- and the passive film at the atomic scale and is a good reference for this study. This was the first time that Cl^--induced dissolution of step edges was proposed at the atomic scale. For the Cu_2O film [25], there are different lattice structures, electronic properties, and oxidation states from those of the NiO film [26], which may result in different forms of interaction with Cl^-.

For the second topic, the work of our research group has proposed a method combining DFT calculations with electrochemical experiments to characterize the corrosion resistance of the passive film by the parameter of the diffusion coefficient of $V_{Cu}^{'}$ [27,28]. First, both the calculations and experiments were performed on the Cu_2O film at ambient temperature. The calculated results show that the diffusion coefficient $V_{Cu}^{'}$ is of the order of $10^{-17}\,cm^2\,s^{-1}$ [27], which is consistent with the experimental results achieved by the electrochemical impedance spectroscopy (EIS) measurements and Mott-Schottky analyses. The same study was also performed on the passive film of copper subsequently formed in solutions containing sulfide at 298, 323, and 348 K [28]. Both the DFT calculations and electrochemical experiments demonstrate that the diffusion coefficient of $V_{Cu}^{'}$ is within the range of 10^{-15}–$10^{-14}\,cm^2\,s^{-1}$. The above two studies only focused on the inherent properties of the passive film, with no investigations on the effect of Cl^-, which is discussed in this study.

In this study, the Cu_2O film was first formed on pure Copper polarized in a solution without Cl^-. Subsequently, a certain amount of NaCl was added to the solution. The samples were subjected to EIS, X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) measurements before and after immersion to identify the thickness and component distribution of the film. To further investigate the mechanism of passivity breakdown, first-principles calculations were conducted to define the interaction between Cl^- and Cu_2O film at the atomic scale. The structural relaxations, thermodynamic energies, and electronic properties of the adsorption and insertion of Cl^- on or into the Cu_2O film were calculated. The effect of the point defect in the Cu_2O film was also considered. The formation energies and diffusion coefficients of $V_{Cu}^{'}$ in each layer of Cu_2O film were calculated to evaluate the thermodynamic and dynamic properties. The effect of surface $V_{Cu}^{'}$ on the adsorption and insertion of Cl^- was also studied for comparison with the defect-free structure.

2. Computational and experimental methods

2.1. Thermodynamic calculations and band structures

The first-principles [29] calculations were performed using the VASP 5.4 [30,31] software. A (2 × 1) Cu_2O (111) supercell was used for the calculations of the structural relaxation and electronic properties. A value of a 15 Å vacuum layer between surfaces was included to prevent interactions between periodic images of the adsorbates and surfaces. Considering the dispersive forces and van der Waals interactions of H_2O molecules, the optimized van der Waals functional Becke 86 (optB86-vdW [32]) was chosen to describe the interactions between H_2O molecules and the Cu_2O surface, which tended to exhibit the smallest errors for most systems investigated. As a correction for localized (strongly correlated) electrons, within the simplified DFT + U approach, on-site Coulomb terms were added [33]. A U–J value of 6 eV was used, which has been proven to be suitable for the Cu_2O system [34]. The convergence of electronic iterations was 1.00×10^{-5} eV using the normal (blocked Davidson) algorithm and reciprocal space projection operators. The user-defined plane-wave cutoff energy was 520 eV. An explicit k-mesh of 2 × 4 × 1 was used. The adsorbates and uppermost third layers were allowed to relax, and the bottom two layers were fixed. Band-structures were calculated by a hybrid functional in the Heyd-Scuseria-Ernzerhof (HSE) framework [33]. HSE06 is expected to underestimate the quasiparticle band gap by no more than 10% [35,36]. The post-processing of the optimized structures was constructed by VESTA [37].

2.2. Dynamic calculations

A (2 × 2) Cu_2O (111) supercell containing 120 atoms was used to calculate the diffusion coefficient $V_{Cu}^{'}$. The molecular dynamics (MD) calculations were performed using the Perdew-Burke-Ernzerhof form of the gradient approximation functional based on DFT for describing the interactions [38]. First, a canonical ensemble (NVT) was performed at 298 K with a time step of 1.0 fs until the potential energy was moving within a span of 1.5 eV for a time of 0.3 ps. Next, the system was thermalized with a constant-temperature and constant pressure (NPT) ensemble for 1 ps (time step = 1.0 fs) with an initial temperature of 298 K and external pressure of 101 kPa. The convergence of electronic iterations was 1.00×10^{-4} eV using the very fast (RMM-DIIS) algorithm and real space projection operators. The user-defined plane-wave cutoff energy was 520 eV, and the explicit k-mesh was 1 × 1 × 1.

2.3. Experimental materials and methods

2.3.1. Experimental materials

Pure copper (99.999%) was studied. The test solution consisted of a borate buffer solution (pH = 9.05), which was prepared using the analytical reagents $0.05\,mol\,L^{-1}$ H_2BO_3 and $0.075\,mol\,L^{-1}$ $Na_2B_4O_7$, and deionized water.

2.3.2. Electrochemical tests

The cyclic voltammetry (CV) and EIS tests were conducted using a traditional three-electrode cell and a 2273 electrochemical system. A platinum (99.99%) plate with an area of 6 cm^2 and Ag/AgCl electrode functioned as the auxiliary electrode and reference electrode, respectively. The working electrode consisted of a pure copper rod with a diameter of 6 mm, which was connected to a copper wire via welding, and subsequently, embedded in epoxy resin. The specimen was polished using various grades of emery paper, and then, polished to a mirror finish with 0.25-μm pastes (the paste type was diamond). Subsequently, the working electrode was cleaned using ethanol and distilled water, successively. Prior to electrode immersion in the solution, the solution was deaerated with high-purity N_2 (99.999%) gas for more than 2 h and was subjected to a continuous flow of high-purity N_2 gas during the subsequent experiments. Prior to each experiment, the specimen was polarized at −1.2 V for 5 min to remove the air-formed oxide film. The specimen was polarized at the film formation potential for 12 h, and the potential was determined by CV curves, whose scanning rate was $20\,mV\,s^{-1}$ from −1.1 V to reversal potentials of 1 V and −0.02 V. The EIS measurements were also conducted within a borate buffer solution of pH 9.05 at the open circuit potential; the measuring frequency was varied from 100 kHz to 10 mHz, using a perturbation of 10 mV.

2.3.3. Component and thickness analyses

To determine the components of the passive film formed on copper under the potentials selected by the CV tests, Raman spectra were recorded using the 633 nm line of an Ar^+ excitation laser using an inVia-Reflex micro-Raman system with a spectral resolution of $2\,cm^{-1}$. The power of the laser (3.5 mW) was set to 50% and focused on the sample by an Olympus microscope with a 50 × long working distance objective.

XPS and AES were used to examine surface composition and depth profile of the passive film and to estimate the change in the thickness of the passive film. XPS measurements were carried out using Al-K_α X-rays (1486.6 eV, width 100 eV), and the pressure in the XPS analysis chamber was $\sim 1 \times 10^{-10}$ mbar. To examine the thickness of the passive film, the samples were etched by Ar^+ bombardment with an

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