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Short-range effect at the semi-coherent metal/its native oxide interface

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ABSTRACT

Fundamentally understanding the variations of atomistic and electronic properties at the interface of metal/its native oxide systems plays a critical role in many important technological processes and applications, such as oxidization, corrosion, chemical catalysis, fuel reactions, and thin-film process. Here, we have adopted the representatively semi-coherent $Cu_2O(111)$/Cu(100) interface and demonstrated, by first-principles calculations on energetic and electronic structures of a total 9 candidate interfacial models, that the preferred geometries (i.e., that having the largest adhesion energy) are those possess the shortest interfacial distance between O terminated Cu_2O and substrate Cu. Using several analytic methods, we have thoroughly characterized the variation of electronic states from the interface to Cu_2O constituent, and determined that the large degree of charge accumulation at the interface is at the expense of depletion of charge in both substrate Cu and neighboring Cu (Cu_2O) to the interfacial O atoms. Strikingly, in Cu_2O the conducting states appear only in monolayer proximal to Cu_2O/Cu interface, as well, the second layer remains in semi-conducting state as its bulk, indicating a short-range effect in electronic properties induced by Cu substrate. The theoretical calculations provide insight into the complex electronic properties of the functional Cu_2O/Cu interface, which was quite difficult to observe by experimental methods alone. The unique properties are of practical importance for further understanding and improvement of such a promising class of metal/native oxide interface at the atomic scale.

1. Introduction

Metal/its native oxide interfaces at nanoscale are currently a subject of intensive research because of their potential for a wide range of technological applications and fundamental scientific importance. The notable interests poured into the metal/native oxide interface could be mainly classified to three aspects: i) Metal/native oxide interfaces have been extensively adopted for the fundamental study of early stage oxidation of metal and oxide film growth on metal surfaces [1,2]; ii) The native oxide layer, which is naturally formed typically at the practically harsh environments and at the situation of device miniaturization or artificially grown, plays a critical role in affecting the performance of metal device. So the elucidation of interfacial interactions is one essential issue for evaluating the property of the metal devices [3]; iii) The native oxide generally exhibits the intriguing properties strikingly different from its metal counterpart, the relationship between the thickness and properties of oxide is the other issue for better manipulating the devices with metal/native oxide interface.

Taking copper (Cu) for example, which is one of most widely used metals, it exhibits intriguing properties, such as very high thermal and electrical conductivity, rendering it vastly applicable for diverse fields, for instance, that relating to: conductor, a constituent of various metal alloys, etc. General findings indicate that oxidation proceeds from chemisorption of atomic oxygen to the formation of an oxygen-deficient induction layer, mainly composed of cuprous oxide (Cu_2O) [4–6]. Consequently, a detailed investigation of Cu_2O/Cu interface could not only attain new fundamental understanding on this class of technologically important metal/native oxide interfaces but also provide a guidance in better designing and manipulating the fabrication of nanodevices [7–11].

Experimentally, Zhou and co-authors [12–20] observed the direct growth of Cu_2O during the oxidation of stepped Cu surface using *in-situ* atomic-resolution electron microscopy observations. They found that the oxidation occurred on flat terraces of Cu, with

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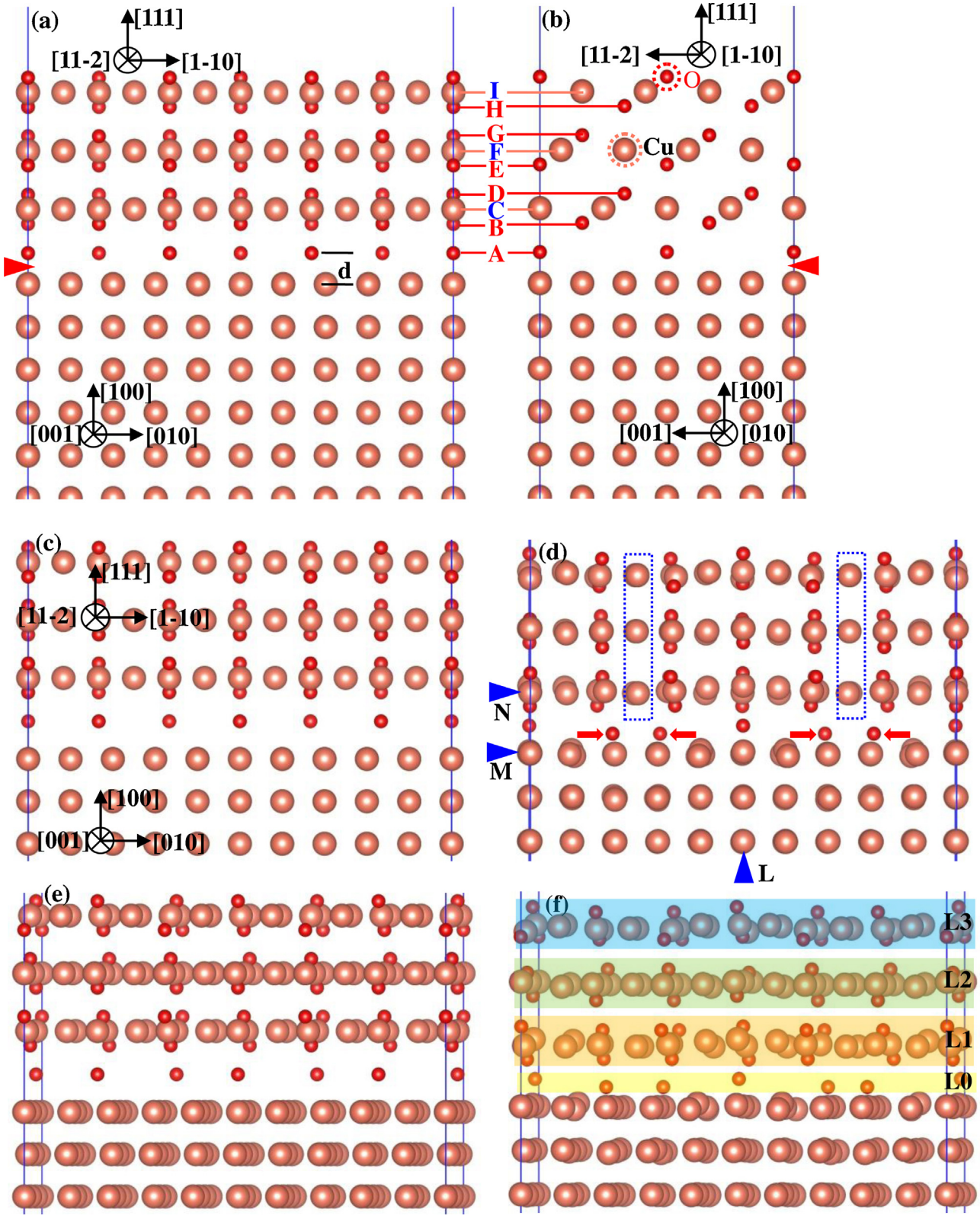

Fig. 1. Schematic structures for $Cu_2O(111)$ [11-2] || Cu(100)[001] interface from view (a) Cu_2O[11-2] (or Cu [001]) and (b) Cu_2O[1-10] (or Cu[010]). The position of interface is marked by a red wedge and the *d* represents the distance of interface. Different termination of Cu_2O is labeled from A to I, producing the nine candidate interfacial models. (c) unrelaxed and (d) relaxed interface for G-terminated Cu_2O and Cu, and (e) and (f) show the corresponding slightly tilted models for clarity. The bottom portions of the interface have been omitted. The shaded areas in (f) are adopted to represent the vicinity of Cu_2O in Fig. 4 PDOS. The L, M and N denote the positions for choosing the horizontal or vertical plane for charge density and difference in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).