Applied Surface Science 394 (2017) 472–478

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full length article

Atomic species recognition on oxide surfaces using low temperature scanning probe microscopy

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ARTICLE INFO

Article history:
Received 3 September 2016
Received in revised form 19 October 2016
Accepted 21 October 2016
Available online 22 October 2016

PACS:
07.79.Cz
07.79.Fc
07.79.Lh

Keywords:
Scanning probe microscope
Oxide surface
Atomic recognition

ABSTRACT

In scanning probe microscopy (SPM), the chemical properties and sharpness of the tips of the cantilever greatly influence the scanning of a sample surface. Variation in the chemical properties of the sharp tip apex can induce transformation of the SPM images. In this research, we explore the relationship between the tip and the structure of a sample surface using dynamic atomic force microscopy (AFM) on a Cu(110)-O surface under ultra-high vacuum (UHV) at low temperature (78 K). We observed two different c(6×2) phase types in which super-Cu atoms show as a bright spot when the tip apex is of O atoms and O atoms show as a bright spot when the tip apex is of Cu atoms. We also found that the electronic state of the tip has a serious effect on the resolution and stability of the sample surface, and provide an explanation for these phenomena. This technique can be used to identify atom species on sample surfaces, and represents an important development in the SPM technique.

1. Introduction

Scanning probe microscopy (SPM) technologies, such as scanning tunneling microscopy (STM) and dynamic atomic force microscopy (AFM), are basic methods currently used in nanotechnology, and are expected to be used in future bottom-up processes, such as the surface characterization, control, and recognition of atoms or molecules at nano atomic scales [1,2]. STM, which is based on the electric tunneling current effect between the conductive tip and the sample surface, can electrically observe individual atoms/molecules, characterize or analyze the electronic nature around surface atoms/molecules, and even manipulate individual atoms/molecules on conductor/semiconductor surfaces [3]. However, STM cannot be applied to insulator surface imaging due to the large band gap between the tip and the sample surface. In contrast, AFM directly measures the forces induced by the tip apex and sample surface, and is a unique mechanically-based atomic tool that can deal with conductor, semiconductor, and insulator surfaces [1,4]. Both AFM and non-contact AFM (NC-AFM) have rapidly developed into powerful surface tools at the atomic/molecular scale because of their high resolution, force and elastic deformation detection capabilities, and measurement of the distribution of potential and charge [5–8].

Tip termination is also a key technique used in SPM measurements [9–11]. Sharp and specific tip apexes of cantilevers in AFM and STM can be used to discriminate between chemically different atoms on a surface structure, and to examine the different geometric and electronic structures of surfaces with real-space atomic resolution [12,13].

In the past, STM/NC-AFM imaging and force spectroscopy have been frequently used to investigate metal oxides, and especially Cu (110)-O, which is of great importance in many fields [16–19], including microelectronics and catalysis [14,15]. The Cu (110)-O surface develops different phases depending on its degree of exposure to oxygen. At low oxygen exposures (less than 100 L, $1\,\mathrm{L} = 1.33 \times 10^4$ Pa s), a p(2×1) phase forms [20], and as the exposure increases the p (2×1) structure endures[21–23] until at 2/3 oxygen coverage, at an exposure in the order of 10^3 L, a transient c (6×2) structure occurs [16,23,24]. At an exposure of 10^4–10^5 L, the surface is predominantly covered with the c (6×2) structure [24]. The p (2×1) phase, which is generally accepted as an “add row”

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http://dx.doi.org/10.1016/j.apsusc.2016.10.140
0169-4332/

(AR), has been studied extensively, both theoretically and experimentally. The c (6×2) phase, which has a double AR structure, exhibits additional copper atoms in every second row, known as “super” copper atoms, bound between two oxygen atoms [20,25]. As a result, oxygen atoms bonded to copper atoms are raised slightly out of plane and buckled in toward the super-Cu atoms. These are called “high” or “buckled” oxygen atoms. The arrangement of Cu and O atoms on the Cu (110)-O surface significantly influences its properties [22–28].

Some researchers have performed experiments using STM and AFM under ultra-high vacuum (UHV) conditions to clarify the relationship between the tip apex and the observable atoms on the Cu (110)-O surface in different phases. They found that the state of the tip apex (i.e., the sharpness of the tip and atomic species of the tip apex) plays a crucial role in STM and AFM atomic-scale imaging [24]. Theoretical and experimental NC-AFM results under UHV at low temperature have shown that when the tip apex is an O atom, the protrusions on the p (2×1) and c (6×2) surfaces are Cu atoms, and when the tip apex is a Cu atom, the protrusions on the p (2×1) and c (6×2) surfaces are O atoms. Surprisingly, in STM and AFM experiments at room temperature, no protrusions of O atoms can be observed using any tip apex. This is because the interaction and dipole moment between the tip apexes and atoms differ [23,29,30]. Also, the sharpness of the tip apex determines the resolution on the Cu(110)-O surface, so when the tip apex is sharp enough, it is possible to achieve sub-atomic resolution of the sample surface [31,32].

In this study, we successfully used NC-AFM at 78 K under UHV conditions to observe the p (2×1) and c (6×2) phases. and mixture structures produced depending on the amount of oxygen exposure. We also confirmed that the species of the tip apex determines the surface structure, and that the sharpness of the tip apex can induce various atomic images on the Cu (110)-O surface. We provide an explanation for these experimental results, and note that this research has important implications for AFM imaging and can also shed light on chemical recognition with respect to the SPM technique.

2. Experimental details

We conducted all experiments using a home-built NC-AFM equipped with a sputter-ion gun operating under a ultrahigh vacuum (less than 5×10^{-11} Torr) and high-pressure oxygen at 75 K, for which the thermal drift was less than 0.05 Å/min.

The Cu (110) substrate had a maximum disorientation of 0.4° and a purity of 99.999% (metal crystals & oxides). We cleaned the Cu (110) surface by repeated Ar^+ ion sputtering (1.4 keV) for 20 min, then annealed it at 500 °C for 40 min for at least 15 cycles. This procedure removed contaminants and residual charges from the surface and yielded atomically flat terraces, which we then imaged with AFM. We then exposed the surface to 2000 L of oxygen at 300 °C. We generated the mixture phases of c (6×2) and p (2×1) on the Cu (110) surface, after which we transferred the sample into the main chamber. The cleaning process and oxygen exposure are illustrated in Fig. 1(a) and (b), respectively.

We used the frequency-modulation technique [33] to detect the tip – sample interaction, and used commercial silicon cantilevers (*n*-doped, 0.01–0.025 Ωcm, Nano world, Switzerland), with a resonance frequency, spring constant, and quality factor of 160 kHz, 40 N/m, and 150,000, respectively, as the sensor, which was set to maintain a constant oscillation amplitude at 5.6 nm. We detected the deflection signal of the cantilever using an optical beam deflection system, and measured the frequency shift of the oscillating cantilever using phase-locked-loop-based commercial electronics (easyPLL plus detector and controller, Nano surf, Switzerland) fed into two loops. In one loop, we used a phase-locked loop (PLL) circuit and automatic gain (AGC) as feedback to maintain constant amplitude and frequency of the cantilever (Nanonis System, SPECS Zurich GmbH, Switzerland). In the other loop, we used the frequency shift ($\triangle f$) of the cantilever to maintain a constant distance between the tip and sample (SPECS, Zurich GmbH).

We cleaned the commercially available Si cantilever by Ar^+ ion bombardment at an energy level of 1.2 keV in situ for 20 min; the radius of the cantilever was less than 10 nm. Both the cantilever and the sample were electrically grounded throughout the experiment.

Initially, the sharp silicon tip was used to scan the CuO surface with large scanning area (100 nm × 100 nm). Then, we confirmed that there are a few Cu-O clusters distributed on the CuO surface. After that, we moved the tip over a specific cluster and intentionally crashed into it. After we confirmed the tip was still stable, a smaller area was scanned with the stable soft contact tip and two different types of images were obtained with respect to variation of the tip apex in the end. We can assume that a Cu-O cluster was terminated the Si cantilever.

3. Results and discussion

The p (2×1) phase, shown in Fig. 2(a), has an alternating/missing row in the (110) direction, where along the (001) rows we confirmed the presence of alternating Cu and O atoms. The p (2×1) phase was formed with an oxygen coverage of 1/2 monolayer (ML). In the c (6×2) phase, oxygen-induced reconstruction occurred at a higher oxygen exposure and shows a double row/missing row structure, in which the Cu and O atoms alternate along the (001) direction, and a missing row is also confirmed in the (110) direction. In every second missing row, additional super-Cu atoms are bonded between two oxygen atoms, which lie higher than the other atoms, as shown in Fig. 2(b). We can recognize the super-Cu atoms by their different and distinguishable ordering from the O atoms on the c (6×2) surface. We can directly distinguish between p (2×1) and c (6×2) structures by their super-Cu and O atoms. The transition between p (2×1) and c (6×2) has been confirmed by Sun et al. and Shohei Kishimoto et al. [33,34].

At oxygen exposures of 2000 L on the Cu (110) surface, p (2×1) and c (6×2) phases of oxidized Cu (110) are formed. Fig. 3 shows atomic-resolution topographic images of (a) a large area, (b) an enlarged image from (a), and (c) a cross-section. The oxidized Cu (110) shown in Fig. 3(a) has a step height of approximately 2.43 Å, which we confirmed by the cross-section labeled in Fig. 3(c). We clearly observed Cu atoms with a spacing of 5.10 Å, which corresponds to the distance between the super-Cu atoms in the c (6×2) phase (Fig. 3(b)).

Fig. 4(a) shows the tip formation of types I and II, and two scanning images of the same area of the c (6×2) phase are shown in Fig. 4(b)and (c), respectively. We confirmed that when a pure silicon tip is used to soft crash several times into a Cu-O cluster on the mixture surfaces of the p (2×1) and c (6×2) phases by controlling the variation frequency $\triangle f$ until contact (soft contact), the Cu-O cluster is pushed onto the tip apex, and two types of tip are formed—type I and type II. When scanning the sample surface using a type-I tip, we observed a bright spot at the expected positions of the super-Cu atoms. As a result, we can see that the surface species of the tip apex is oxygen. Using the same method, when scanning the sample surface using a type-II tip, two close spots are imaged instead, located at around the same position as in type I. We attribute these spots to the two high-O atoms. As a result, the surface species of the tip apex is Cu [16,35].

To further demonstrate the dependence of the tip apex species on image contrast, we decreased the tip – sample separation by decreasing the frequency shift from −17.5 Hz to −20.0 Hz using the