Applied Surface Science 258 (2012) 9623–9628

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Ultrathin films of Cu on Ru($10\bar{1}0$): Flat bilayers and mesa islands

J. Brona*, R. Wasielewski, A. Ciszewski

Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9, 50-204 Wrocław, Poland

ARTICLE INFO

Article history:
Received 23 March 2012
Received in revised form 29 May 2012
Accepted 31 May 2012
Available online 8 June 2012

Keywords:
Metallic surfaces
Ruthenium
Copper
Scanning tunneling microscopy (STM)
Low-energy electron diffraction (LEED)
Auger electron spectroscopy (AES)

ABSTRACT

The Cu/Ru($10\bar{1}0$) adsorption system was investigated by STM, LEED and AES. Cu was deposited at room temperature (RT) and 800 K, with the coverage ranging from a fraction up to 4 bilayers (BL). The first two Cu BL grow in the bilayer-by-bilayer mode. Their structure is pseudomorphic and does not depend on the temperature. For coverage higher than 2 BL, Cu deposited at elevated temperature forms three-dimensional islands in mesa shape with Cu(111) facets on their tops. The facets and the substrate are epitaxially oriented with Cu(111)||Ru($10\bar{1}0$) and Cu[$01\bar{1}$]||Ru[$1\bar{2}10$]. Obtained results can be helpful in search for an optimal method of Cu deposition onto Ru in the damascene process in microelectronics, and could be also of interest to catalysis.

1. Introduction

The research on the Cu/Ru($10\bar{1}0$) adsorption system reported in this paper is interesting from three points of view: catalysis, microelectronics, and pure science in the context of heteroepitaxy. Ru-based catalysts find many important applications, e.g. in synthesis [1] and decomposition [2] of ammonia. Ultrathin metallic films grown on top of a metallic substrate can modify its physical and chemical properties. For example, the catalytic activity of Ru(0001) in hydrocarbon conversion reactions in the presence of a submonolayer coverage of Cu can be enhanced 40 times, as compared to the clean Ru surface [3]. There are numerous bimetallic surfaces that have applications in catalysis [4,5]. Single crystals used as model systems are helpful in understanding industrial catalysts [6]. Recently, a Cu/Ru(0001) system served as a model catalyst in studies on the reactions of methanol [7] and the epoxidation of propylene [8]. Corrugated surfaces often have different properties than the close-packed ones. For example, the Ru($10\bar{1}0$) surface exhibits a higher activity toward CO [9] and H_2 [10] electrooxidation than the Ru(0001) one. Therefore, the Cu/Ru($10\bar{1}0$) system can be an interesting model catalyst.

Investigation of Cu/Ru($10\bar{1}0$) can be helpful in search for an optimal method of deposition of Cu on Ru in the damascene process [11] in microelectronics. In this process, a diffusion barrier layer is typically applied to a dielectric substrate. As the trend of miniaturization continues in microelectronic fabrication, the current Ta/TaN diffusion barrier encounters scaling difficulties. Recently, ruthenium has been proposed as a new candidate for the diffusion barrier. Armini et al. have analyzed several systems used in the damascene process and found that the most promising one is copper direct plating on Ru, which allows filling of 7 and 13 nm features for logic and memory, respectively [12]. Currently, research is conducted on the deposition of Cu onto Ru [13–17] in the damascene process. In the first stage of the deposition, one of the desired features of the thin layer of Cu directly placed onto Ru is smoothness [12,18]. The search for new methods of fabricating Ru layer is also carried out. Such layers usually are polycrystalline and consist of (0001), ($10\bar{1}0$), ($10\bar{1}1$), and ($10\bar{1}2$) facets [16,19–22].

In contrast to the Cu/Ru(0001) adsorption system which has been intensively investigated [23–41], the research on the Cu adsorption on Ru($10\bar{1}0$) was limited to measurements made in the context of the CO adsorption [42]. Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), thermal desorption (TD), and work function (WF) measurements were applied. It was revealed that the first two layers were flat and pseudomorphic. In this paper we report on the research on the structure and morphology of a Cu adsorbate on Ru($10\bar{1}0$) for the coverage up to 4 bilayers (BL). We applied scanning tunneling microscopy (STM), LEED, and AES. Our aim was to find out whether ultrathin pseudomorphic Cu films grow as geometric or physical layers, and follow the adlayer for increasing Cu coverage until fcc(111) planes, natural for copper, are formed. Since the temperature might affect the growth of

* Corresponding author.
E-mail address: jacekb@ifd.uni.wroc.pl (J. Brona).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.05.160

adsorbate, as it has been observed for Cu/Ru(0 0 0 1) [39], in our investigation copper was deposited on the substrate at both room temperature (RT) and 800 K.

2. Materials and methods

The experiment was performed in an ultrahigh vacuum (UHV) STM system built by Omicron NanoTechnology with the base pressure below 10^{-10} Torr. STM experiments were done with home-made tungsten tips. LEED and AES experiments were carried out with a four-grid spherical energy analyzer with a retarding field. Measurements were performed on a single-crystal sample of Ru(1 0 $\bar{1}$ 0) cut within 0.4° accuracy (delivered by Mateck). The sample was cleaned by several cycles of oxygen adsorption and thermal desorption in order to remove the surface carbon. Residual traces of oxygen were removed by flashing to 1800 K. This procedure resulted in a surface for which no contaminants were detected by AES, and a sharp (1 × 1) LEED pattern was obtained. We estimate that the amount of a potential contaminant that we could detect by AES was not more than 5% of 1 BL (about 0.1×10^{15} atoms/cm^2). During deposition at 800 K the sample was heated by the radiation of a hot tungsten wire placed behind the sample. Higher temperature was obtained by electron bombardment. The temperature of the sample was measured by the Minolta Cyclops 153A infrared thermometer. Cu was deposited by evaporation from a home-made electron beam evaporator with a Mo crucible. The rate of Cu deposition was 0.3 BL per min. Calibration of Cu source was based on Auger uptake curves. We define 1 BL as a physical monolayer (composed of two geometric monolayers in case of the hcp(1 0 $\bar{1}$ 0) face) with atomic density of 1.73×10^{15} atoms/cm^2. During deposition of Cu the sample was kept either at RT or at 800 K. In the latter case, measurements were carried out after cooling the sample down to RT.

3. Results and discussion

Fig. 1a and b shows STM images of the clean Ru(1 0 $\bar{1}$ 0) surface and the substrate covered with 0.6 BL Cu deposited at RT, respectively. The comparison between these images reveals that Cu adsorbate forms flat elongated structures rectangular in shape. Longer sides of these structures lie along the [1 $\bar{2}$ 1 0] direction. Cross sections (Fig. 1c) reveal 0.23 ± 0.02 nm height of the steps for both the substrate and the adsorbate. It means that the step edges have a height of 1 BL. There are two possible terminations of the hcp(1 0 $\bar{1}$ 0) surface: long and short (see Fig. 1d). In the case of the long surface termination, the distance between the topmost and the second geometric layers of Ru crystal is equal to 0.156 nm. If the surface is short-terminated, the distance is equal to 0.078 nm. By considering geometric arguments, one can intuitively conclude that, in case of a real crystal, the short termination is favored. Density functional theory (DFT) calculations confirm that the short-terminated Ru(1 0 $\bar{1}$ 0) surface is energetically favored by 4.1 eV/nm^2 [43] or 4.0 eV/nm^2 [44] over the long-terminated surface. It suggests that the surface of a real crystal is indeed short-terminated and that the steps at the Ru(1 0 $\bar{1}$ 0) surface are 0.23 nm high. This was confirmed by LEED IV measurements [43]. Therefore we assume that the surface in reported here experiments is short-terminated. In our STM measurements, we have

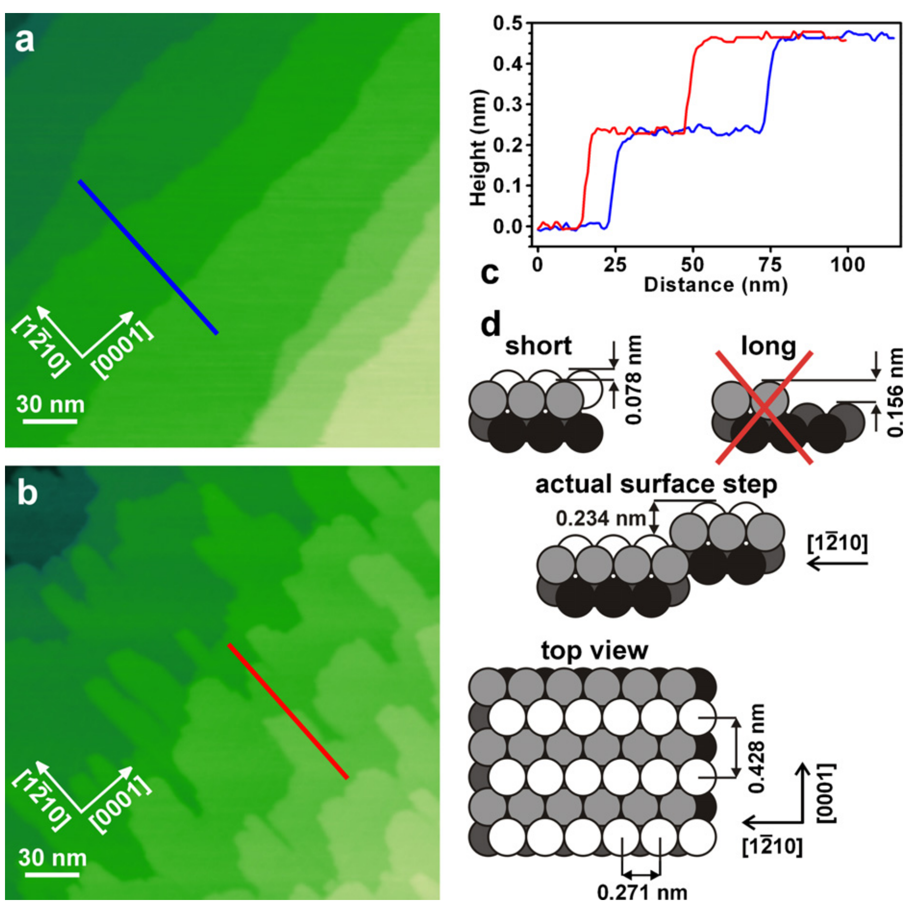

Fig. 1. STM image of (a) the clean Ru(1 0 $\bar{1}$ 0) surface (U = +2.0 V, I = 0.11 nA) and (b) the substrate covered with 0.6 BL of Cu deposited at RT (U = +1.9 V, I = 0.12 nA). (c) Cross sections along the lines indicated in parts (a) and (b). (d) Model of the Ru(1 0 $\bar{1}$ 0) substrate: cross section along the [1 $\bar{2}$ 1 0] direction and the top view.