



# Nanoscale characterization of copper oxide films by Kelvin Probe Force Microscopy



Tobias Berthold <sup>a,\*</sup>, Guenther Benstetter <sup>a</sup>, Werner Frammelsberger <sup>a</sup>, Rosana Rodríguez <sup>b</sup>, Montserrat Nafria <sup>b</sup>

<sup>a</sup> Deggendorf Institute of Technology, Edlmairstr. 6 + 8, 94469 Deggendorf, Germany

<sup>b</sup> Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Barcelona, Spain

## ARTICLE INFO

Available online 8 February 2015

### Keywords:

Kelvin Probe Force Microscopy  
Contact Potential Difference  
PeakForce  
Copper oxidation

## ABSTRACT

In this work PeakForce Kelvin Probe Force Microscopy (PF-KPFM) at ambient environment is used to characterize both oxidation states of copper (Cu) surfaces, cupric oxide CuO and cuprous oxide Cu<sub>2</sub>O, with high lateral resolution. Characteristic values of the Contact Potential Difference were obtained for the copper oxide states. By this means, PF-KPFM measurements enabled to distinguish between the different types of Cu oxide with nanometer resolution and to correlate the oxidation states to local topography features. It was even possible to identify single oxide grains on top of the Cu surface. As a result, PF-KPFM is able to address the needs for nanoscale characterization methods in semiconductor manufacturing or other related technologies where the local oxidation behavior of copper is a critical issue.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Copper (Cu) has become an important metallization material in semiconductor manufacturing. Notwithstanding the importance of Cu metallization, wire bonds are still predominantly made of gold wires due to their key advantages such as flexibility and reliability [1]. In comparison to gold, copper is cheaper and it possesses an increased thermal and electrical conductivity. However, one of the main drawbacks of Cu is that the surface is subject to oxidation, even at room temperature. Chuang et al. [2] demonstrated that the oxidation of the Cu bond pad influences the quality and the reliability of the bond contact. Ho et al. [3] observed that, even within the same lot of identically processed wafers, some contact structures are bondable, whereas others are not and associated their observation to the oxidation behavior of the Cu bond pad. Few researchers have addressed the problem of the Cu oxidation by coating the copper surface with an additional metal layer or a thin organic self-assembled monolayer (SAM) in order to prevent the oxidation [3–6]. However, due to the elevated bonding temperature the surface oxidation cannot simply be neglected and has to be taken into account. For manufacturing of reliable and predictable copper wire bonds and the development of respective industrial processes additional research is necessary to analyze the oxidation behavior of the bond pad and the role of possible other contaminations.

The characterization methods predominantly used in recent studies have been X-ray diffraction and X-ray photoelectron spectroscopy [2,7,8]. Even though these methods are suitable for detecting the oxidation states of the Cu pad, they allow only limited lateral resolution

due to the excitation by an X-Ray beam and therewith a correlation between small topography features and oxidation state remains unstudied. PeakForce Kelvin Probe Force Microscopy (PF-KPFM) [9] has the potential to address these needs. PF-KPFM is a modification of the common Kelvin Probe Force Microscopy (KPFM) [10–12] and enables the measurement of the Contact Potential Difference (CPD) of material surfaces with high lateral resolution at ambient environment. The CPD value is related to the work function of the surface. However, a direct characterization of the oxidation state by comparing a theoretical CPD value of the Cu oxide with the measured CPD value was not possible. Local variations of surface properties and related work function values and, as reported by Sugimura et al. [13], the presence of a surface water layer in ambient environment, which shields the CPD value, are reasons for this observation. Therefore, we used Energy Dispersive X-Ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) as reference measurements and correlated the CPD values achieved by PF-KPFM with the corresponding Cu oxide state detected by EDX and FTIR. As a result, PF-KPFM measurements in air enabled to distinguish between the different types of Cu oxide with nanometer resolution and to correlate the oxidation states to local topography features. In this work we show that the combination of different measurement techniques facilitates the advanced characterization of the oxidation behavior of the Cu surfaces, the investigation of thin oxide films and the correlation of local topography changes to the corresponding oxidation state.

## 2. Experimental details

In this work the key method used for the characterization of thermally grown Cu oxides is PF-KPFM. However, as PF-KPFM performed

\* Corresponding author. Tel.: +49 991 3615 513; fax: +49 991 3615 599.  
E-mail address: [tobias.berthold@th-deg.de](mailto:tobias.berthold@th-deg.de) (T. Berthold).

in air environment is subject to diverse disturbances, it is important to validate the data achieved. For this reason EDX and FTIR are employed and are explained in this section.

The schematic cross-section of the Cu test samples used in this study is shown in Fig. 1. The 5  $\mu\text{m}$  Cu was deposited by sputtering and shows a well-defined surface structure (Fig. 2). Individual grains and grain boundaries may clearly be identified and the grains offer a uniform grain orientation Cu(111) measured by Electron Backscatter Diffraction (EBSD). In order to achieve sufficient thick cupric oxide CuO and cuprous oxide Cu<sub>2</sub>O for the EDX and the FTIR investigations the Cu samples were oxidized, according to the literature [14,15], on a heater in ambient air for two hours at 300 °C and for 24 h at 120 °C, respectively. Comparatively thin oxide films were generated by oxidizing for two and five minutes at 200 °C, which is close to real bonding conditions [16]. Prior to oxidation, the samples were chemically cleaned with an aqueous solution of 10% sulfuric acid to remove the native oxide and contaminations and subsequently rinsed with a 1:1 solution of ultrapure water and isopropanol. Except for the measurements the samples were constantly stored in dry air environment (~23 °C, 0% humidity) to prevent surface contamination and to reduce the influence of a water layer on the sample surface.

In this experiment a Zeiss Ultra 55 Scanning Electron Microscope (SEM) equipped with the EDAX Trident system and an Energy Selective Backscatter Detector (ESB) was used to perform EDX, EBSD and Backscattered Electron (BSE) imaging. EDX is able to measure the element content quantitatively and was employed to identify the oxidation state by the ratio of the atomic weight of Cu to oxygen (O). However, this is only applicable for comparatively thick oxides, which were grown purposely for these experiments. For thin oxide layers and small oxide particles in the nm range the capabilities of EDX are limited because of the penetration depth caused by the electron beam. The acceleration voltage used was 3 kV. Based on the SEM parameters we performed a Monte Carlo simulation of electron trajectories using the software tool electron flight simulator (EFS). EFS simulates the electron beam penetration by the energy loss resulting from inelastic collisions in-between individual elastic scattering events [17]. We computed a penetration depth at 3 kV of circa 60 nm for bulk Cu<sub>2</sub>O with a density of 6.0 g/cm<sup>3</sup> and a depth of circa 50 nm for bulk CuO with a density of 6.31 g/cm<sup>3</sup>. For analyzing oxide layers or oxide particles smaller than the calculated penetration depth, the ESB detector was chosen. This detector provides a relative material contrast by BSE imaging and was applied to validate the PF-KPFM results of the comparatively thin oxide layers. EBSD was used to identify the grain orientation of the Cu layer. As the EBSD measurement displayed an amorphous structure of the grown oxides, a discrimination of the Cu oxides by using EBSD was not possible.

In addition to the SEM techniques an additional chemical characterization was performed by reflectance FTIR with a Thermo Nicolet Nexus 470 spectrometer in dry air environment (~23 °C, 0% humidity). The detector is sensitive in the wave number range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> and the incidence angle of the IR beam to the sample was 20°. Since CuO and Cu<sub>2</sub>O show different vibration modes [18], they can be distinguished by FTIR. Thin oxide layers have still a highly reflective surface

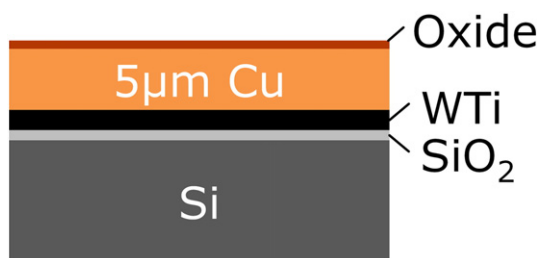


Fig. 1. Schematic x-section of test samples consisting of a 5  $\mu\text{m}$  PVD copper layer on top of a Si base separated by a thin SiO<sub>2</sub> film and a WTi liner.

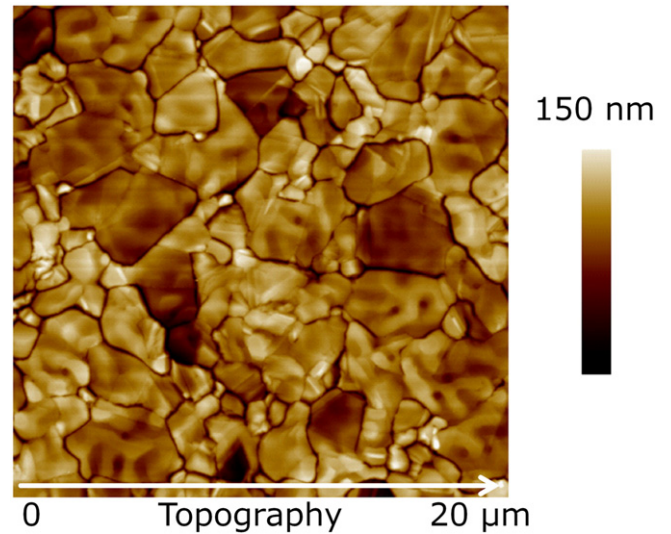


Fig. 2. AFM topography image of the copper surface.

and therefore the absorption area of the IR beam is very low. That limits the usability for detecting thin oxide layers. FTIR was used as an additional validation of the EDX and the PF-KPFM results.

The Atomic Force Microscopy (AFM) measurements were performed with a Bruker Dimension Icon AFM. Beside various standard operation AFM modes, the AFM employed offers the PF-KPFM [9] operation mode, which is able to measure the CPD value. The CPD value constitutes the difference of the work function of the AFM probe tip and the sample. In our setup the measured CPD is defined by the work function of the AFM probe tip  $\Phi_{\text{tip}}$  minus the work function of the sample  $\Phi_{\text{sample}}$ . Thus a  $\Phi_{\text{sample}}$  higher than the  $\Phi_{\text{tip}}$  yields negative CPD values and vice versa. However, a direct characterization of the oxidation state by comparing theoretical and measured CPD values is not possible because the work function of materials shows some variations which are dependent on e.g. crystal structure or surface states and may not be assigned to a single value. Moreover, as the measurements were performed under ambient conditions (~25 °C, 50% humidity), it needs to be taken into account that a water layer may be present on top of the oxide surface and that this water layer influences the CPD value [13]. Compared with frequency modulated (FM)-KPFM mode, PF-KPFM reveals additional mechanical properties such as adhesion and elastic modulus [19] and, most important here, it provides the CPD values with improved sensitivity and repeatability in ambient air [9]. The advantages of PF-KPFM are closely linked to appropriate AFM probe tips with higher quality factor Q and lower spring constant k. We used uncoated silicon probe tips (PFQNE-AL from Bruker AXS) with a nominal spring constant of 0.8 N/m and a resonance frequency of 300 kHz, which are especially designed for PF-KPFM. In order to enhance the reliability of the results and to prevent artifacts due to contaminated or damaged probe tips the measurements were repeated with different probe tips of the same type. The CPD values obtained for thick oxides by PF-KPFM in association with the corresponding validation by EDX and FTIR were taken as basis for the measurements of comparatively thin oxides obtained by the oxidation step at 200 °C.

### 3. Results and discussion

In this study PF-KPFM was used to characterize the oxidation state of thermally grown copper oxide by using EDX and FTIR as reference. The 300 °C oxidized Cu sample exhibited a black surface which indicates that the layer consists of cupric oxide CuO [20]. The copper layer oxidized at 120 °C exhibited a reddish surface which suggests that the oxide layer consists of Cu<sub>2</sub>O [20]. Both observations are in accordance with literature [14,15].

Download English Version:

<https://daneshyari.com/en/article/1664870>

Download Persian Version:

<https://daneshyari.com/article/1664870>

[Daneshyari.com](https://daneshyari.com)