



# Titanium monoxide ultra-thin coatings evaporated onto polycrystalline copper films

R.A. Zárate<sup>a,b,\*</sup>, V.M. Fuenzalida<sup>b</sup>

<sup>a</sup> *Facultad de Ciencias, Departamento de Física, Universidad Católica del Norte Casilla 1280, Antofagasta, Chile*

<sup>b</sup> *Facultad de Ciencias Físicas y Matemáticas, Departamento de Física, Universidad de Chile, Casilla 487-3, Santiago 837-0449, Chile*

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## Abstract

We evaporated polycrystalline copper thin films of thickness between 10 and 100 nm on silicon substrates with their native oxide under ultra-high-vacuum conditions. Some of them were exposed to air for a period ranging from 1 day to 2 weeks. X-ray photoelectron spectroscopy (XPS) revealed a clean copper surface with a trace of oxygen. These films that were exposed to air presented oxides in the state Cu(II), the amount of CuO depended on the time that the film was exposed to air. Subsequently, we deposited TiO ultra-thin films on polycrystalline copper substrates. Both these thin films were formed by electron beam evaporation. XPS spectra showed that the surface of the titanium monoxide (TiO) films was contamination-free. An evaporation of 0.3 nm of TiO reduced the native oxide of the copper substrates from Cu(II) to Cu(I) or Cu(0) and transformed the TiO into TiO<sub>2</sub> at the interface. Low-energy ion spectroscopy showed that the complete coverage of the substrates depends on the thickness of the copper films. For 10 nm copper thin films the complete coverage occurred at 1.5 nm of TiO, and for 100 nm it occurred at 2.0 nm of TiO. In samples exposed to air, the complete coverage occurred at a film thickness slightly higher than those treated under ultra-high-vacuum conditions.  
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## 1. Introduction

Titanium monoxide (TiO) has been proposed as an electrically conducting metallization, for both microelectronics and layered piezoelectric applications [1–3]. TiO is expected to provide a diffusion barrier, similar to RuO<sub>2</sub> [2,3]. Additionally, the

surface of TiO oxidizes immediately in air to TiO<sub>2</sub> [4], providing an anticorrosive coating. This is observed, for example, in alloys that passivate in air with titanium entering mainly as TiO<sub>2</sub> [5]. A potential advantage of this system is that amorphous TiO can be deposited on substrates at room temperature, thus avoiding thermal stresses due to the difference in thermal expansion coefficients.

The growth of transition metals on single-crystal surfaces has been extensively studied, particularly the growth of copper on rutile TiO<sub>2</sub> (1 1 0) [6–10].

\*Corresponding author. Tel.: +56-55-355517; fax: +56-55-355521.

E-mail address: [rzarate@ucn.cl](mailto:rzarate@ucn.cl) (R.A. Zárate).

There is evidence that copper grows on stoichiometric and  $\text{Ar}^+$ -sputtered  $\text{TiO}_2$  (1 1 0) surfaces as three-dimensional clusters and does not react with the substrate [6,7]. The inverse problem, that is, the deposition of oxides on metals, has received less attention. In this case, metal–oxide interactions can substantially modify the properties of ultra-thin oxide films.

Grigorov et al. [2] studied conductive TiO films of 100  $\mu\text{m}$  in thickness, deposited onto Si (1 0 0) by reactive ion beam deposition at low temperature. The RBS measurements showed a low interdiffusion of Si into the TiO films and the resistivity was about 170  $\mu\Omega\text{cm}$ . A study of TiO thin films with lesser thickness than those presented by Grigorov is performed by Chae et al. [3], who studied self-passivated copper evaporating 15 nm of TiO thin films, forming 8 nm of continuous TiO films on the outer surface of the copper. They showed that multilayers  $\text{TiO}/\text{Cu}/\text{TiO}/\text{TiN}/\text{SiO}_2$  exhibited stable electrical passivating properties against Cu diffusion.

Maeda et al. [11] reported on ultra-thin titanium oxide films on Cu (100), prepared by the evaporation of titanium on the oxygen-chemisorbed copper surface and further oxidation in oxygen, concluding that the composition of the oxide was  $\text{TiO}_2$  from the intensity of the  $\text{Ti}2p_{3/2}$  and  $\text{O}1s$  and that the growth mode of titanium oxide was through two-dimensional clusters for the first layer. Wu and Nix reported that  $\text{TiO}_{2-x}$  films deposited on single crystal Cu (100) substrates at 600 K by chemical vapor deposition exhibited low reactivity with the substrate [12]. The oxygen pre-adsorbed on the copper surface is scavenged by the first deposited titanium oxide layers, thus reflecting the fact that the interaction between oxygen and the copper substrate is weak compared with the affinity between titanium and oxygen. In further experiments, copper single crystals were pre-oxidized exposing to  $\text{O}_2$  at 400 K, thus increasing the reactivity between the copper substrate and the titanium oxide. The initial growth appears to give a uniform oxide film (layer by layer or simultaneous multilayer growth) and, above a coverage of 7 monolayers, 3-dimensional crystallite growth begins.

In the present work, we report on the deposition of TiO overlayers evaporated in ultra-high vacuum (UHV) conditions on clean and preoxidized polycrystalline copper substrates. The copper films were freshly deposited on Si (1 0 0), which is solely used as a mechanical support. Copper and TiO were deposited by electron beam evaporation, the partial pressure of oxygen being below  $10^{-6}$  Pa. We report on the interaction between the titanium oxide and the copper substrate in the early growth stages as well as on the growth mode of the TiO ultrathin film, extending our previous results on films evaporated from resistively heated tungsten boats [13].

## 2. Experimental

The starting substrates were (100) oriented silicon wafers with their native oxide. The samples were introduced through a load-lock into the analysis chamber and transferred with a magnetic arm to the preparation chamber, allowing them to position directly above the evaporation source. The substrates were not heated during deposition, although some temperature increase can be caused by the thermal radiation from the evaporation source.

The UHV preparation chamber was pumped with turbomolecular, ion and nitrogen-cooled titanium sublimation pumps, with a base pressure in the range of  $10^{-8}$  Pa. Copper and TiO were evaporated from crucibles in different pockets of a 6-pocket electron beam evaporator (Telemark model 528), monitoring the deposition with a vibrating quartz microbalance (Maxtek model TM400). Copper shot 99.9% (Alfa Aesar #10159), at a working pressure of  $10^{-7}$  Pa was evaporated at a rate around 0.03–0.13 nm/s. TiO was sublimed from TiO pellets (Alfa Aesar #14714) at a pressure in the range of  $10^{-6}$  Pa, mainly due to hydrogen as measured with a mass spectrometer, at a deposition rate in the range of 0.0017–0.0025 nm/s. The quartz monitor was calibrated using a profilometer (TENCOR model ALFA step 500).

The films were analyzed by angle-resolved X-ray photoelectron spectroscopy (XPS) (ARXPS, Phy-

sical Electronics model 1257 system) and by low-energy ion scattering spectroscopy (LEIS). The XPS peaks were referred to the position of the Cl 1s peak at 284.5 eV. All XPS measurements were made collecting the photoelectrons at  $0^\circ$ , a direction coincident with the normal to the surface of the sample, and at grazing emission at  $80^\circ$  from the normal. At  $0^\circ$ , the collected spectra are a superposition of the surface oxide and the material underneath, however, the collected spectra at grazing emission is mainly the surface oxide. The LEIS measurements were performed using  $^3\text{He}^+$  ions at 1 keV. The peak positions were calibrated against standards of pure copper, titanium and titanium oxide. All LEIS measurements were made by collecting the ions at  $0^\circ$  from the normal.

The experiments were performed as follows: copper films either 10 or 100 nm in thickness were evaporated onto silicon wafers, transporting some of the samples to the analysis chamber for LEIS and XPS characterization. One set of these copper films was returned to the evaporation chamber for further deposition of different amounts of TiO, a single TiO deposition on each copper film. A second set of copper films was extracted from the vacuum system and exposed to air for 1–14 days. This treatment produces a thin native oxide layer as shown by XPS. Afterwards, a single TiO deposition was performed on each oxidized copper substrate. Both the sets of samples were characterized by LEIS and XPS after each TiO deposition.

### 3. Results and discussion

#### 3.1. Coating and sealing of the copper-film substrate

Since the substrate is a good conductor and leads to no charge accumulation, LEIS is the most appropriate technique to determine the critical thickness of TiO capable of sealing the copper-film substrate. Fig. 1 shows LEIS spectra of several samples of different thickness of TiO on 100 nm clean copper films. The copper peak disappears after deposition of 2.0 nm of TiO, indicating complete coating. Since the density and formula weight of TiO are  $4.95\text{ g/cm}^3$  and  $63.9\text{ g}$ , the

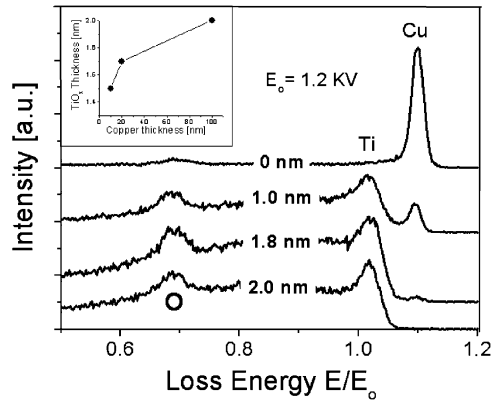


Fig. 1. LEIS spectra of TiO deposited on a 100 nm clean copper film. The copper substrate is no longer visible after deposition of 2 nm of TiO. Inset: amount of TiO sealing the copper substrate as a function of copper thickness.

thickness of a single monolayer is calculated to be 0.27 nm, therefore the critical thickness is around 7 monolayers (ML). This fact indicates that the thin film grew as three-dimensional clusters on the 10 nm as well as on the 100 nm copper films.

Table 1 summarizes the observations on different sets of samples, where the results close to the sealing threshold alone are shown. The following trends are observed:

- (i) In all cases, with or without air exposure, the sealing of the copper-film substrate is achieved by the deposition of 6–8 ML of TiO. Fig. 1. shows the LEIS spectra of the coating of the 100 nm copper film substrate with different thickness of TiO. The complete coverage was reached at 2.0 nm.
- (ii) A slightly smaller TiO thickness is required to seal the thinner copper films, both air-exposed or handled under UHV. We suppose that the sealing depends on the roughness of the copper films, and is expected to increase with the film thickness as it has already been observed in other systems [14].
- (iii) There is no clear correlation indicating the effect of air exposure on the amount of TiO required for sealing.
- (iv) In order to test if the samples were sealed, they were exposed to a pressure of 0.1 Pa during

Table 1  
Summary of LEIS results showing sealing of the copper substrate

Copper thickness (nm)	Environment	TiO thickness (nm/ML)	Sealing of the copper substrate (LEIS)
100	UHV	1.8/7	Almost complete
100	UHV	2.0/7	Complete
100	Air	1.8/7	Almost complete
114	Air	2.1/8	Complete
20	UHV	1.8/7	Complete
10	UHV	1.5/6	Complete
10	UHV	1.8/7	Complete
10	Air	1.5/6	Almost complete <sup>a</sup>
10	Air	1.5/6	Complete

<sup>a</sup>This sample was first coated with 1.2 nm and an additional 0.3 nm were deposited on a second run.

5 min in the introduction chamber. The LEIS spectra recorded on these samples did not change over and above a trace of contamination, i.e., the samples after this experiment continued to be sealed.

### 3.2. Reduction of the surface copper oxide by TiO

Even at temperatures close to room temperature the deposition of TiO on oxidized copper surfaces is highly reactive. The copper oxide layer is reduced when the TiO thin layer is deposited on preoxidized copper substrates.

The curve at the top of Fig. 2 represents the Cu2p high-resolution photoelectron emission of a preoxidized copper film, with the Cu2p<sub>3/2</sub> peak at 932.2 eV, acquired collecting the photoelectrons emitted normal to the surface. The shake-up feature near 945 eV is characteristic of CuO. The comparison with a reference spectrum of pure CuO [15] indicates that the observed shake-up intensity is smaller than in pure CuO. Therefore the observed Cu2p spectrum is presumably the superposition of unoxidized copper and/or Cu<sub>2</sub>O (dominant signal at 932.2 eV) and CuO (shake-up seen between the Cu2p<sub>1/2</sub> and Cu2p<sub>3/2</sub> peaks of Fig. 2).

The bottom curve of Fig. 2 exhibits the same Cu2p photoemission after deposition of around one monolayer (0.3 nm) of TiO. The shake-up feature is now absent, indicating that the CuO was reduced. It is worthwhile noticing that this reduction occurs close to room temperature, and

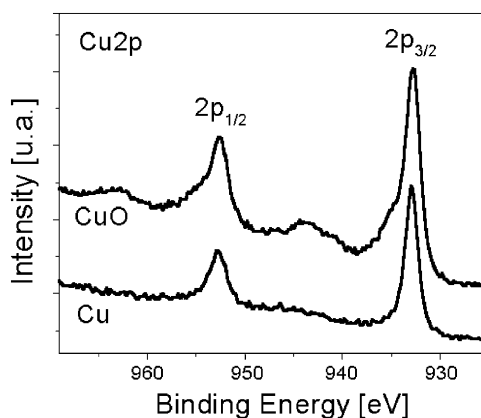


Fig. 2. XPS spectra of preoxidized copper substrate. Top: copper substrate exposed to air for two weeks showing the shake-up of CuO. Bottom: after deposition 0.3 nm of TiO.

that the critical thickness to cover the copper-film substrate is around six times larger. The single monolayer TiO deposit is able to scavenge the oxygen from the CuO and reduce it even if it does not wet the substrate, as indicated by the LEIS measurements. These results are consistent with our previous report on resistively evaporated films [13].

## 4. Conclusions

We prepared TiO ultra-thin films deposited on polycrystalline copper thin films previously evaporated on silicon single crystals, (100) oriented.

Both materials were deposited by electron beam evaporation in a UHV system. Using low-energy ion scattering (LEIS or ISS), we found that the TiO thin films grew in three-dimensional clusters and that sealing of the copper-film substrate was achieved by 6–8 ML of TiO, i.e., 2.0 nm approximately. The thickness of the sealing depended on the thickness of the copper films, which we attribute to a surface roughness that increases with the copper film thickness. We did not find a clear correlation indicating the effect of air exposure of Cu films on the amount of TiO required for sealing. X-ray Photoelectron Spectroscopy (XPS) spectra revealed that copper and titanium oxide thin films were contamination free after evaporation, but the copper films exposed to air presented oxides in the state Cu(II). TiO films deposited on pre-oxidized copper surfaces exhibited reactive adsorption, reducing Cu(II) to Cu(I) or Cu(0).

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