

Protection of Cu from Oxidation by Ta Capping Layer

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Abstract: X-ray reflectometry (XRR) and X-ray photoelectron spectroscopy (XPS) measurements (core levels and valence bands) were made of Cu thin films that were prepared and coated by capping Ta layers with different thicknesses (5, 10, 15, 20, and 30 Å), and are presented. The XRR and XPS Ta 4f-spectra revealed a complete oxidation of the protective layer up to a thickness of 10 Å. From the thickness of the capping layer of 15 Å, a pure Ta-metal line appeared in the XPS Ta 4f-spectrum, the contribution of which increased up to 30 Å. The XPS Cu 2p-spectra of the underlying copper layer revealed the oxidation with the formation of CuO up to a thickness of the Ta-layer of 10 Å. Starting from a thickness of 15 Å, the complete protection of the Cu layer against oxidation was ensured during exposure to the ambient atmosphere.

Keywords: films; XPS; X-ray reflectometry; tantalum; oxidation



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1. Introduction

Copper has the highest conductivity of any non-precious metal. This, combined with its high ductility, medium strength, and ease of joining makes copper the first choice as a conductor for electrical applications. Another equally important use of copper is its application as a sink hat to remove heat in various electronics elements (transistors, diodes, etc.). All these parameters are strongly influenced by surface oxidation of copper in the ambient atmosphere and heating [1,2]. For example, the loss of thermal conductivity in copper due to oxidation can reach 24% [3]. Another potential problem is that the copper oxide layer is not self-protective, meaning the copper can become readily oxidized even at low temperatures. Therefore, the study of copper oxidation and the development of methods to prevent the oxidation of copper surfaces are especially important in microelectronic packaging and has become a matter of increasing interest in the last years. Different ways of protecting Cu surfaces from oxidation are discussed in the literature and involve either a protection layer [4], alloying [5], or ion implantation [6]. The present work was undertaken: (i) to determine whether the Ta capping layer is an effective method of copper surface protection, and (ii) to estimate the minimal thickness of the Ta-capping layer for the protection of Cu from oxidation.

2. Experimental and Calculation Details

A Cu (100 Å) film and a series of Cu(100 Å)/Ta(x Å)/(x = 5, 10, 15, 20 and 30 Å) bilayers were grown by UHV magnetron sputtering onto glass substrates at room temperature using the MPS-4000-C6 vacuum magnetron sputtering machine (ULVAC, Chigasaki, Japan). In the following, we named these samples as Cu, Cu/Ta5, Cu/Ta10, etc. The base pressure in the growth chamber was 10^{-6} Pa. Sputtering was performed in an atmosphere of extremely pure argon at a pressure of 0.1 Pa. The substrate was rotated during sputtering to ensure uniform film thickness across the entire surface of the substrate. The main process

parameters for sputtering nanostructures were as follows: magnetron power—100 W; substrate rotation frequency—8 rpm; and substrate temperature during sputtering—room temperature. Cu and Ta layers were grown with rate ca 1 Å/s. Subsequent oxidation was conducted in air under natural conditions.

The layered structure of the samples was characterized ex-situ with X-ray reflectometry. The measurements were performed with the PANalytical Series 2 diffractometer using Co K α radiation ($\lambda = 1.79$ Å). The incident beam was formed with the parallel beam mirror using 1/32° divergence slit. The diffracted beam was then formed with the parallel plane collimator together with the flat crystal monochromator allowing an equatorial acceptance of the beam of 0.27° and a beam collimation of 0.1 mm, respectively. Data analysis was performed with X'Pert Reflectivity software.

PHI 5000 VersaProbe spectrometer (ULVAC Physical Electronics, Chanhassen, MN, USA) equipment were used for conducting XPS measurements with a high spatial- and energy-resolution. This spectrometer utilizes a classic X-ray optical scheme with a spherical quartz monochromator and energy analyzer working over the range of binding energies from 0 to 1500 eV, and it includes an electrostatic focusing system and magnetic screening. The achieved energy resolution was no worse than $\Delta E \sim 0.5$ eV for an Al K α radiation (1486 eV). The spot size was 200 μm and the X-ray power load delivered to the sample was less than 50 W. A dual-channel neutralizer was used to compensate for the local charging of the sample under study due to the loss of photoelectrons. All samples under study were previously kept in the vacuum chamber for 24 h under rotary vacuum pumping. The pressure in the analytical chamber did not exceed 10^{-7} Pa during measurements. The spectra were processed using ULVAC PHI MultiPak Software 9.9.0.8. The XPS spectra were then calibrated relative to the reference energy value of the carbon 1s core level at 285.0 eV.

The electronic structure calculations for Ta and Ta₂O₅ were conducted using the density functional theory (DFT) as it was implemented in Wien2k code [7]. The generalized gradient approximation (GGA) by Perdew et al. [8] was employed. The number of k-points was chosen to be 200 (in the irreducible part of the Brillouin zone). The cutoff energy to separate the valence and core states was taken to be -6 Ry. The spin-orbit coupling was taken into account using the second variational method [9].

For calculations of the Ta's structure, this was characterized by the cubic lattice (space group: Im-3m), with lattice parameters of $a = b = c = 3.30256$ Å, and angles of $\alpha = \beta = \gamma = 90$ deg were used, respectively [10]. The structure where all Ta ions were in equivalent positions was chosen for the calculation of Ta₂O₅: the space group C2/c (number 15), $a = 12.7853$ Å, $b = 4.8537$ Å, $c = 5.5276$ Å, $\alpha = \gamma = 90$ deg, and $\beta = 104.264$ deg. More details can be referred in [11].

3. Results and Discussion

Experimental XRR curves and their corresponding fitting curves for the Cu film, and the samples of the series with different thicknesses of the Ta capping layer (from 5 to 30 Å) are shown in Figure 1. From XRR data analysis, it was found that there was a Ta oxide layer at the top of Cu/Ta samples, as well as an absence of the Ta layer and the appearance of the Cu oxide layer near the Cu/Ta interfaces in the samples with a nominal Ta thickness of up to 10 Å. The presented layers' thicknesses for Cu and Cu/Ta samples as determined from XRR data fitting are displayed in Table 1.

Figure 2 shows the results of the measurements of the XPS survey spectra of the Cu film and Cu/Ta bilayers differing in the thickness of the Ta capping layer (from 5 to 30 Å), and in Table 1 the compositions of their surfaces, determined from these spectra are also illustrated. It follows from the data that in the studied samples, there were only the lines of copper, carbon, tantalum, and oxygen, and there were no impurities observed.

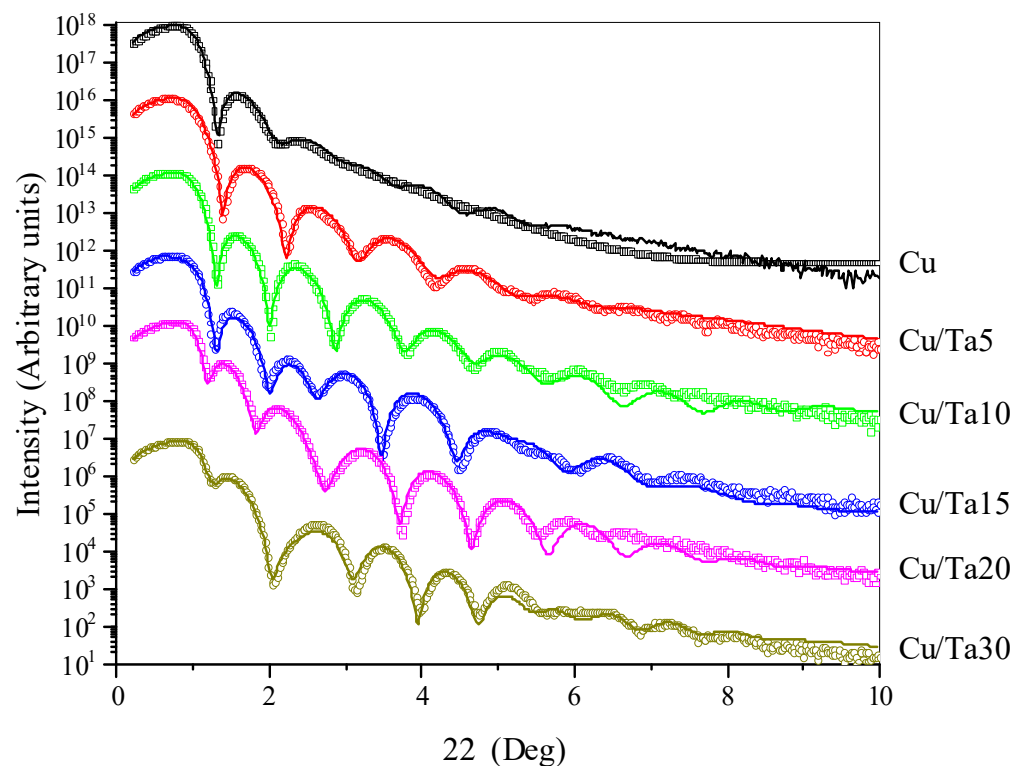


Figure 1. XRR experimental data and corresponding fitted curves for the Cu film and Cu/Ta bilayers.

Table 1. Layers' thicknesses (in Å) as determined from XRR and surface composition (in at. %) as determined by XPS.

Sample	Layers' Thicknesses (Å)				Surface Composition (at. %)			
	Cu	CuO	Ta	Ta ₂ O ₅	C	O	Ta	Cu
Cu	85	15	0	0	48.7	27.7	-	23.6
Cu/Ta5	81	14	0	8	54.7	30.1	6.5	8.7
Cu/Ta10	83	11	0	12	40.4	42.7	12.9	40.
Cu/Ta15	90	0	7	9	25.6	53.8	19.7	0.9
Cu/Ta20	98	0	11	12	27.9	50.1	21.0	1.0
Cu/Ta30	84	0	21	12	25.4	51.6	22.7	0.3

The XPS Ta 4f-spectra measured with a high-energy resolution makes it easy to determine the oxidation of the Ta-metal, as the binding energies of the Ta 4f spectra of the metal and oxide differ by almost 4.9 eV [12]. These spectra measured for the studied samples clearly showed (see Figure 3a) that the Tantalum capping layer was almost completely oxidized to Ta₂O₅ for the thicknesses of 5 and 10 Å, respectively, and that the contribution of the non-oxidized metal appeared only at a layer thickness of 15 Å, and subsequently increased significantly with a thickness of 20 and 30 Å. This result was deemed to be consistent with the XRR results. This interpretation of the XPS Ta 4f spectra was confirmed by their comparison with the results of the DFT calculations. In Figure 3a, Ta 4f levels in the pure metal and Ta₂O₅ were shown along with their experimental spectra. The XPS Cu 2p spectra from the underlying copper layers behaved as according to these data (as shown in Figure 3b). Therefore, by comparing these spectra with the spectra of as prepared Cu sample and reference samples (CuO and Cu), it follows that the thickness of the tantalum layer 5–10 Å does not protect the underlying copper layers from oxidation, and the data obtained indicate the formation of CuO in the surface layer of the Cu/Ta5 and Cu/Ta10

samples. On the other hand, an increase in the Ta capping layer to 15 Å was found to be already sufficient to protect the copper layer from oxidation. This was evident by the high-energy shift of the Cu 2p spectrum until it coincided with the spectrum of the Cu-metal.

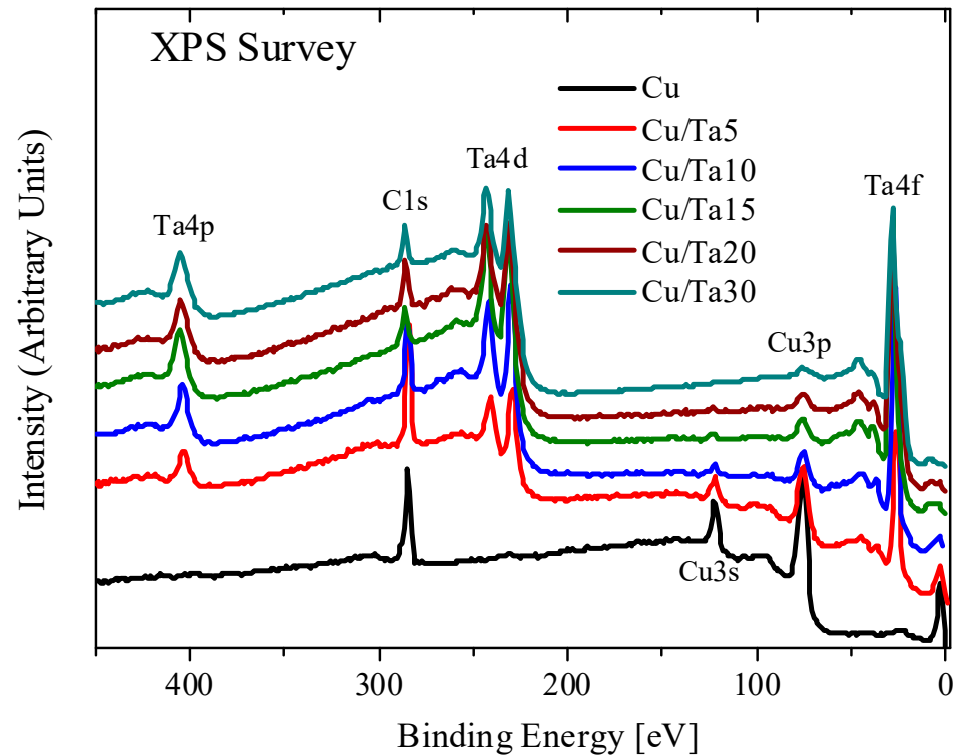


Figure 2. XPS survey spectra.

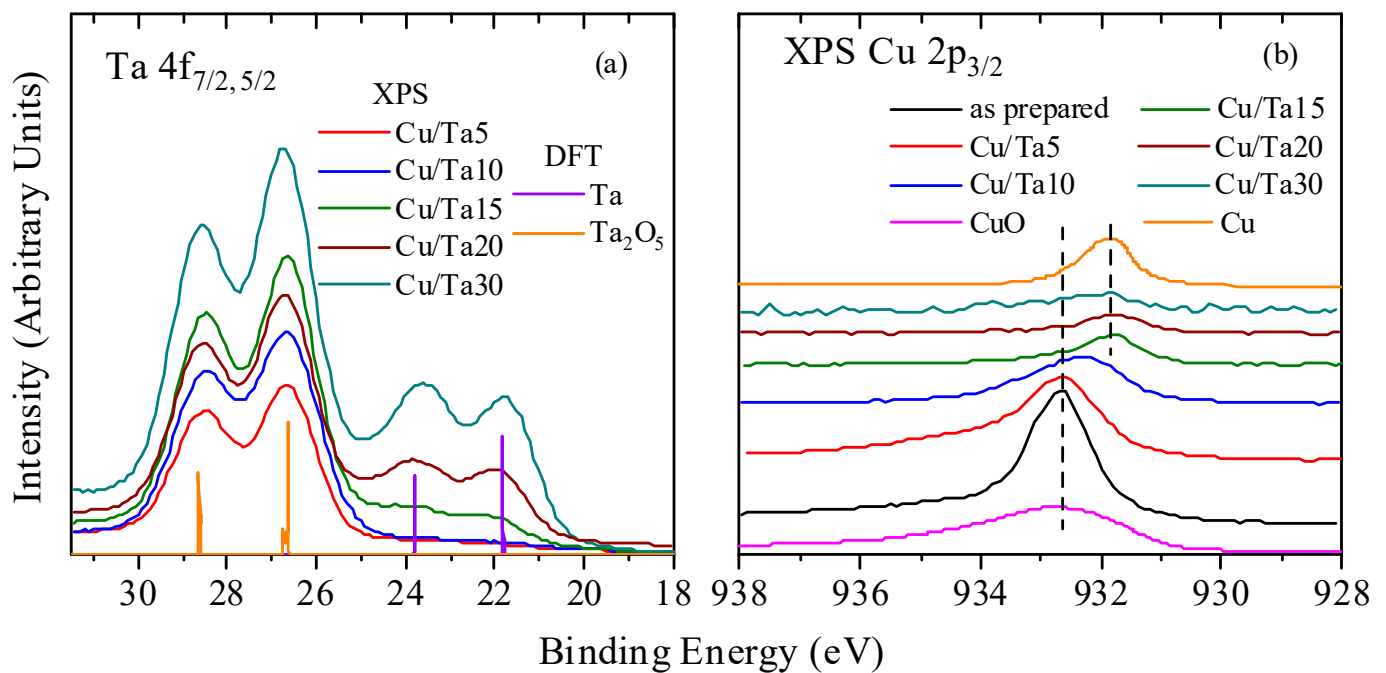


Figure 3. XPS Ta 4f spectra in the Cu/Ta layers and the DFT calculations of Ta and Ta₂O₅, (a) and the XPS Cu 2p_{3/2} spectra of the Cu/Ta layers and reference samples (b).

The results obtained in the study of the XRR curves and XPS spectra of the core levels were also confirmed by measurements of the spectra of the XPS valence bands (VB)

(Figure 4). As shown by the XPS VB spectra of reference samples (Cu (b), CuO (a), Ta (d), and Ta₂O₅ (c)) the energy shifts between the metals and oxides were quite sufficient to characterize the oxidation states of the atoms of the components in the Cu/Ta layers. From the data shown in Figure 4, it follows that for a layer thickness of 5 and 10 Å, the contribution of CuO to the formation of the valence spectra of Cu/Ta was quite large. It practically disappeared at a Ta layer thickness of 15 Å. Simultaneously, the contribution from Ta and Ta₂O₅ increased. With a Ta layer thickness of 30 Å, we already observed a superposition of contributions from copper, tantalum, and tantalum oxide. Therefore, it follows from these spectra that even with an increase in the thickness of the protective layer from 5 to 10 Å, a small contribution from the pure metal appeared in the XPS valence band spectra. However, from the thickness of 15 Å in the XPS valence band spectra, the contribution from the Cu oxide was completely absent, and in this respect, the XPS VB spectra also testified to the high protective properties of Cu with a tantalum layer of 15 Å thick. As followed from our measurements, the thickness of the capping Ta layer from 15 Å and above ensures the presence of an unoxidized protective layer. This is essential for maintaining the thermoelectric properties of copper. Despite the fact that tantalum and copper are insoluble, tantalum oxide interacts with copper, and could worsen its thermoelectric properties [13]. On the other hand, at a film thickness of 15 angstroms or more, the retention of metallic Ta can contribute to the preservation of thermoelectric properties.

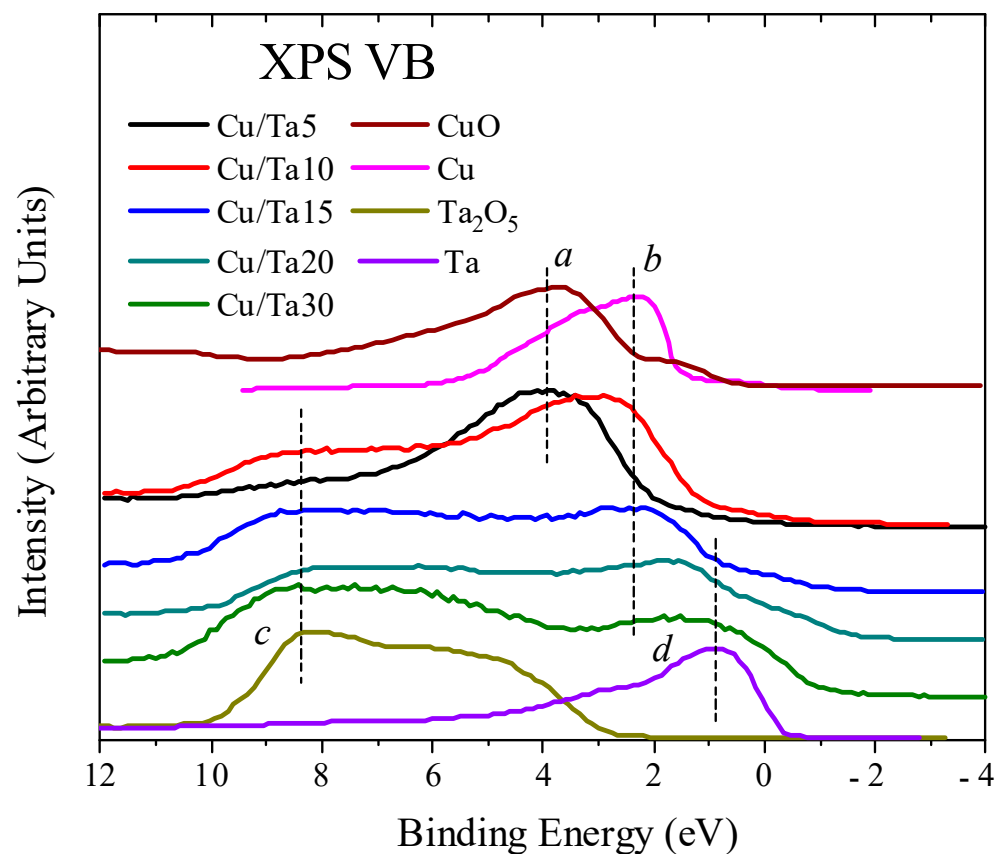


Figure 4. XPS valence band spectra.

4. Conclusions

Thus, the conducted study showed the high efficiency of the Ta layer to protect the underlying copper layers from oxidation when exposed to air. When varying the thickness of the Ta layer, it was found that the minimum thickness of the protective layer at which copper was fully protected from oxidation is 15 Å.

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