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Thickness dependence of the optical constants of oxidized copper thin films based on ellipsometry and transmittance*

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Thin oxidized copper films in various thickness values are deposited onto quartz glass substrates by electron beam evaporation. The ellipsometry parameters and transmittance in a wavelength range of 300 nm–1000 nm are collected by a spectroscopic ellipsometer and a spectrophotometer respectively. The effective thickness and optical constants, i.e., refractive index n and extinction coefficient k, are accurately determined by using newly developed ellipsometry combined with transmittance iteration method. It is found that the effective thickness determined by this method is close to the physical thickness and has obvious difference from the mass thickness for very thin film due to variable density of film. Furthermore, the thickness dependence of optical constants of thin oxidized Cu films is analyzed.

Keywords: thin film, optical constants, thickness, copper

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1. Introduction

Copper has been extensively used to replace aluminum as the interconnect material for ultra-large scale integration (ULSI) devices due to its low resistivity, high thermal conductivity, excellent electron migration resistance, and easy deposition. This application has increased the requirements for characterizing the physical properties of copper thin film. Particularly, the optical property related to dielectric constant is an important factor to determine the performance of the ULSI device.[1,2] However, it is difficult to accurately measure the optical constants of ultrathin absorbing films by traditional optical methods.[3]

Metallic materials suffer oxidation in ambient condition. The oxidation of copper has been studied under various experimental conditions;[4–14] most of them focused on the oxidation kinetics under high temperature. In contrast, the study on oxidation of copper is rarely reported at room temperature. Boggio has investigated oxidation behaviors of single crystal Cu at room temperature for different oxygen pressures and proposed an oxidation model.[4] Suzuki *et al.* have investigated the native oxide layer on the surface of ultra-high purity Cu by using angle-resolved X-ray photoelectron spectroscope (XPS).[5] However, for ULSI technology it is very important to study the oxidation behaviors of not only bulk material but also thin film for copper. Considering the fact that the properties of ultrathin films are very different from those of bulk material due to surface microstructure and oxidation, it is desirable to have an accurate characterization of the optical properties of Cu thin films in ambient condition rather than bulk copper in ideal conditions. Oreilly *et al.* have studied the oxidation behaviors of Cu films in a temperature range from 50 °C to 150 °C.[6] Iijima *et al.* have examined the effect of purity on the native oxidation of Cu and the oxidation rate law of the Cu films below 250 °C.[7] But the influence of thickness on the film optical property was not taken into account in these studies. In fact, when a thin Cu film is exposed to the air, the oxidation rate is very fast in the first few seconds and then becomes so low that the films can be regarded as a relatively stable system.[1,7] At native oxidation condition in stable state, the most important factors influencing the physical properties of Cu film are thus the thickness and microstructure that are determined by the grain size and oxidation layer.[15,16] So it is very important to figure out the relationship between thickness and optical constants of oxidized copper film in ambient condition for quality improvement of ULSI devices.

The present work aims to study the thickness dependence of optical properties of Cu thin films related to their surface microstructures and oxidations in ambient condition by using ellipsometry combined with transmittance iteration method. The mass thickness, effective thickness, and physical thickness are all obtained and compared with each other. Thickness dependence of effective optical constants of oxidized copper thin film at room temperature is analyzed. A three-layer model is proposed for the structure of oxidized copper thin film and

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thickness of each layer is obtained.

2. Experiment

2.1. Film preparation

Copper thin films were fabricated by using electron beam evaporation. Cu target of 99.999% purity was evaporated onto pre-cleaned quartz glass substrates in a vacuum of 1.0×10^{-5} Pa. The mass thickness of the evaporated thin film is determined by a quartz crystal resonator positioned inside the evaporation chamber. The evaporation rate was about 0.02 nm/s. To study the dependence of structural and optical properties on film thickness, a series of thin films with different thickness values were prepared by controlling the evaporation time.

2.2. Characterization

An X-ray photoelectron spectroscope (MTA ATOMKI, ESA-31 spectrometer) was employed to analyze the composition of the oxidized copper in the film. The surface topography was measured by using an atomic force microscope (AFM) in the tapping mode (SII NanoTechnology Inc., NanoCute). The transmittance spectra in a wavelength range from 300 nm to 1000 nm for Cu films deposited on quartz substrates were measured at normal incidence by a double-beam spectrophotometer (Shimazu Co., Inc. SolidSpec-3700). Ellipsometric spectra in a range from 300 nm to 1000 nm were collected at incident angles of 58° and 68° with a rotating-polarizer ellipsometer (J. A. Woollam Co., Inc. M-2000U). The measured ellipsometric spectra combined with transmittance spectra were used to calculate the optical constants of thin films as well as to determine the film thickness iteratively.

3. Results and discussion

In the present work, the ellipsometry iterated with transmittance method is employed to determine simultaneously the film thickness and optical constants for Cu thin films. The detail of this method has been described elsewhere.[17,18] This method is under the assumption of the uniform film, although this assumption is usually considered not to be true for an ultrathin film that may be formed by distributed islands on substrate surface. However, the spot diameter of optical beam in measurement is about a few millimeters, which is much more than the sizes of islands on a nano-scale. So the film can be regarded as homogeneous on a macro-scale. The same optical constants measured at different positions of the sample also support the assumption. Therefore, we define here an effective thickness which satisfies both the ellipsometry equation and Hadley equation.[19] Similarly, the effective optical constants can also be obtained by solving equations.

3.1. Thickness

Film thickness is obtained by three different methods. The mass thickness is determined by quartz crystal resonator. The effective thickness is determined by ellipsometry iterated with transmittance method as mentioned above. And the physical thickness is determined by direct step height measurement using the AFM. The measurement results by different methods are given in Table 1. When the thickness is greater than 15 nm, the thickness values determined by three methods accord with each other. However, for ultrathin film the mass thickness value is significantly smaller than the effective thickness and physical thickness. It is reasonable if the fact is considered that the initial growth of the copper film is in the form of individual islands which would present lower density than that of the bulk material. With thickness increasing, the density would increase due to close packing of atoms. By averaging, the value of the effective thickness is thus larger than the mass thickness which is estimated from the density for close packing of atoms. When film becomes thicker, the averaged film density approaches to the bulk material density gradually; thus, the thickness values determined by the three methods accord better with each other. In fact, the surface layer having a lower density always exists even for a thick film. This explains why mass thickness values are always less than the effective and physical thickness values even if the thickness decreases down to 20 nm. The comparison results in Table 1 indicate that the present optical method can effectively characterize the thickness values of ultrathin films. This lays also the solid foundation for studying the effective optical constants and oxidations of ultrathin copper films.

Table 1. Comparisons of the values of the measured mass thickness, effective thickness, and physical thickness among different samples.

Mass thickness/nm	Effective thickness/nm	Physical thickness/nm
1.9	5.3	5.8±0.6
2.6	6.5	6.4±0.5
3.3	7.7	7.9±0.6
3.8	7.9	8.0±0.6
5.2	9.1	9.2±0.6
6.2	9.7	9.6±0.5
7.1	10.0	11.3±0.5
9.5	13.1	11.8±0.5
14.3	15.6	15.4±0.6
19.0	21.0	21.1±0.4
28.5	28.9	28.2±0.6
38.0	39.1	37.2±0.5

3.2. Effective optical constants

Figure 1 shows the X-ray photoelectron spectrum (XPS) of a representative oxidized copper film with an effective thickness of 7.9 nm. As for Cu_2O, the Cu^+ $2p_{3/2}$ peak at about 932.4 eV and the Cu LMM transition at 570 eV can be clearly seen in the inset of Fig. 1, while the Cu^{2+} $2p_{3/2}$ peak position at about 933.2 eV and the Cu LMM transition at 568.5 eV

for CuO cannot be found.[20] So the XPS analysis reveals that only Cu_2O is detected and CuO is hardly produced on copper surface at room temperature, which is in accordance with the previously reported results.[9,21] Then the influence of CuO on the effective optical constants can be neglected in the sequent analysis.

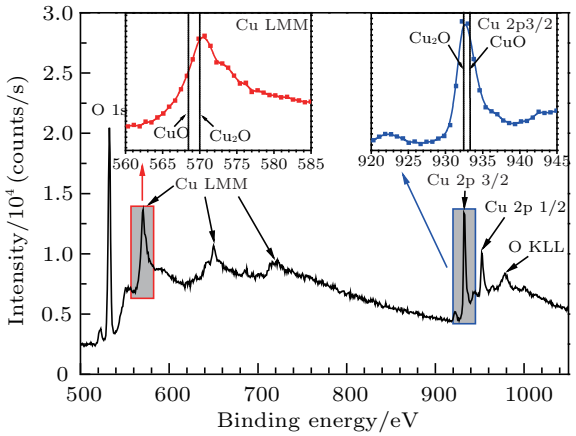


Fig. 1. (color online) X-ray photoelectron spectrum of oxidized copper film. The insets show the XPS core level spectrum of Cu 2p 3/2 and Cu LMM Auger transition.

The dependences of the effective optical constants, n and k, on the wavelength for various thickness values are shown in Fig. 2. The optical constants of bulk Cu and Cu_2O materials from a database[22] are also shown in Fig. 2 for comparison. It is clearly seen that optical constants of the thicker film become close to those of bulk Cu material while those of thinner film are closer to those of bulk Cu_2O material. The film with 10 nm in thickness displays the non-metallic behavior because the value of refractive index is larger than the extinction coefficient in a range of 600 nm–1000 nm (Fig. 2). For films thicker than 10 nm, the extinction coefficient in the infrared region increases linearly with film thickness increasing, which also indicates an obvious metallic behavior. Figure 2 clearly demonstrates a general variation trend with increasing thickness, that is, how the effective optical constants, n and k, of Cu_2O change to those of bulk copper material.

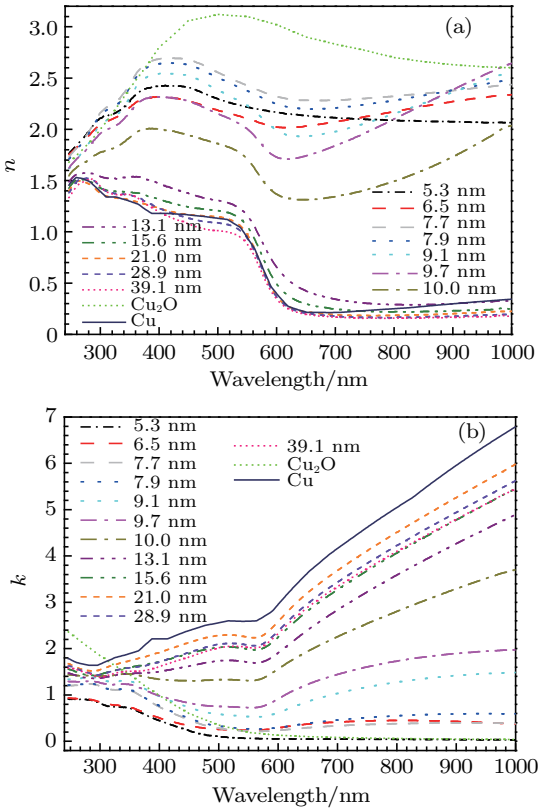


Fig. 2. (color online) Dependences of the refractive index n (a) and extinction coefficient k (b) on wavelength for different Cu film thickness values.

Figure 3 shows the film thickness dependences of optical constants at a wavelength of 633 nm. There is an obvious difference in optical constant between the oxidized copper thin film and the pure bulk copper. The intersection of refractive index and extinction coefficient clearly indicates that the percolation threshold for $n = k$ is about 10 nm; above this percolation threshold the material displays metallicity.[23] The product of n and k is also shown in Fig. 3, which gives a measure of the absorption of the film.[24] The absorption has thus a maximum value when the thickness value of film is close to the percolation threshold.

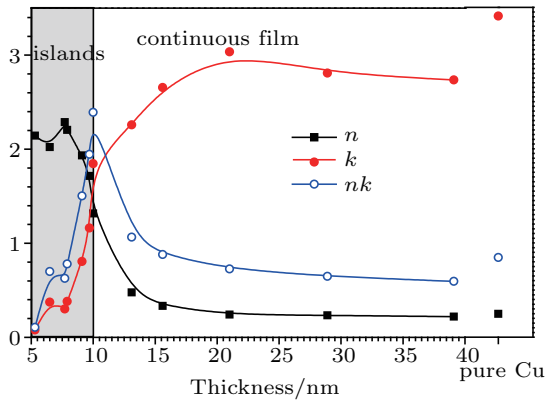


Fig. 3. (color online) Thickness dependences of optical constants at 633 nm.

Figure 4 displays AFM images of the copper films for three different effective thickness values: 5.3, 9.1, and 13.1 nm. The images show that these ultrathin films do not form a smooth uniform layer. Instead, they all consist of nanoparticles grown from nanoislands. For the film in a thickness of 5.3 nm, the islands are individually separate from each other and there exist some obvious interspaces between them on substrate. Some interspaces are marked by white circles in Fig. 4. Increasing the thickness to 9.1 nm, the islands are connected to form nanoparticles which cover the entire substrate surface with smaller interspaces. But the metallic behavior of bulk copper does not appear due to insufficient copper atoms on the substrate. For a thickness of 13.1 nm the substrate is completely covered; the metallic behavior starts to appear above percolation threshold at 10 nm

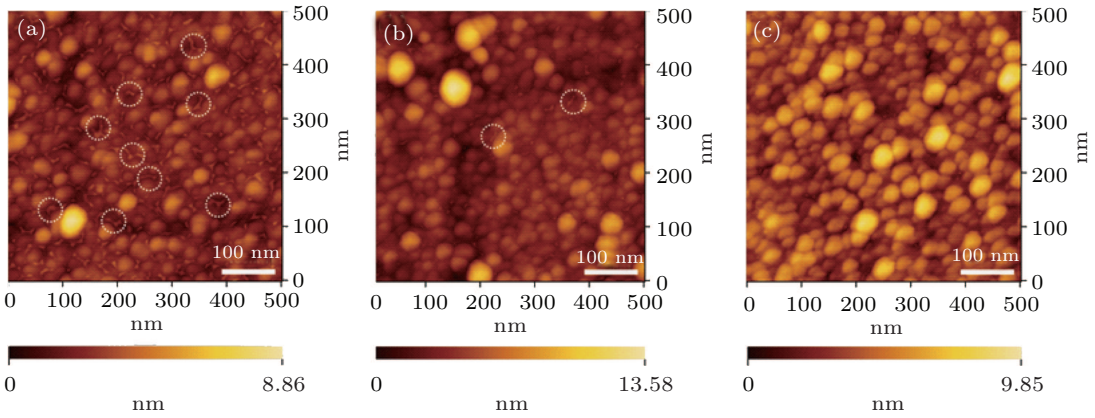


Fig. 4. (color online) AFM images (500 nm×500 nm) of Cu films with effective thickness values of (a) 4.3 nm, (b) 9.1 nm, and (c) 13.1 nm.

as can be seen from Figs. 2(b) and 3, the value of k becomes quite large although the metallicity is still reduced as compared with the bulk copper because of surface oxidation. The AFM images indicates that the percolation threshold occurs somewhere between 9.1 nm and 13.1 nm. This conclusion accords well with the value determined from the optical constants.

When the thickness is below 10 nm, the relationship between optical constants and thickness becomes complicated. Film growth process should be taken into consideration in analyzing the variation mechanism of optical constants. A detailed discussion has been given in previous work.[18]

4. Oxidized layer

In order to understand the influence of oxidation on optical property of ultrathin Cu films, we employ a layer-by-layer growth model as schematically shown in Fig. 5. The thickness of oxidized layer is determined by spectroscopic ellipsometry analysis based on a three-layer model, i.e., rough-Cu_2O/Cu_2O/Cu model. In the calculation process, optical constants of each material in the respective layer are cited from the literature.[22] The copper layer thickness d_{Cu}, Cu_2O layer thickness d_{oxide}, and surface roughness d_R are adjusted so that the calculated spectra are close to the measured spectra. Here, the surface roughness is modeled by mixing the optical constants of surface material (Cu_2O) and 50% air (i.e. $n = 1$ and $k = 0$) as shown in Fig. 5. The results show that this simple 3-layer model proves to work successfully for copper films thicker than 10 nm. The thickness of each layer is given in Table 2.

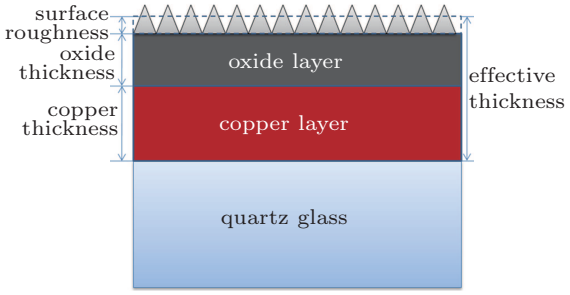


Fig. 5. (color online) Schematic illustration of 3-layer model for oxidized Cu layer on quartz substrate.

The total thickness of copper layer, Cu_2O layer, and surface roughness accords well with the effective thickness obtained by the ellipsometry iterated with transmittance method. Besides, the variation in thickness of oxidized layer attracts our attention: the Cu_2O layer thickness firstly decreases and then increases with increasing effective thickness of film. To explain this abnormal behavior, the oxidation process should be taken into consideration.

After an oxide layer is formed between copper and oxygen, the oxide growth is controlled by the transport of copper ions from the metal to the oxide/oxygen interface through the oxide layer, driven by chemical gradient. Generally, there are two kinds of diffusion mechanisms. One mechanism is defect-related diffusion such as grain boundary diffusion.[25,26] Atomic migration in a grain boundary can be treated as a random walk of atoms in a periodic quasi-two-dimensional (2D) system, which is a fast-diffusion mechanism. The other mechanism is lattice diffusion which is commonly seen in most single crystalline materials.

Table 2. Estimated layer thickness values for samples with different effective thickness values.

Effective thickness/nm	d_{Cu}/nm	d_{oxide}/nm	d_R/nm	$(d_{Cu}+d_{oxide}+d_R)$/nm
13.1	8.60±0.01	1.57±0.02	1.14±0.04	11.32±0.07
15.6	10.96±0.01	1.52±0.02	2.27±0.03	14.75±0.06
21.0	17.59±0.02	1.28±0.02	2.08±0.03	20.95±0.07
28.9	22.23±0.04	2.83±0.02	3.21±0.04	28.27±0.10
39.1	29.55±0.09	3.91±0.02	4.16±0.06	37.62±0.17

In the case of our experiments, the optical measurements were performed in 24 h after sample preparation; then the samples were stored in a relatively dry environment. One week later we performed another set of ellipsometry and transmission spectrum measurements on the same sample and observed little change of data. Therefore, the major mechanism which controls the effective optical constants of thin Cu films should be a fast diffusion mechanism which is dominated by defect-related grain boundary diffusion. The surface of copper nanograins was oxidized to Cu_2O as soon as the specimen was exposed to air. The oxidation of inner copper was so slow that it can be neglected at room temperature. So the oxidation level of copper thin films will largely depend on surface area other than exposure time.

Considering the above fact, we can understand the abnormal change of the effective extinction coefficient when the effective thickness is bigger than 20 nm. In fact, the measured effective optical constants are contributed by both Cu and Cu_2O. Reducing thickness of Cu_2O layer can cause a slight increase of extinction coefficient by considering the fact that the extinction coefficient of Cu_2O is much lower than that of bulk Cu. We infer that the decreasing of Cu_2O layer, while film thickness decreases from 10 nm to 20 nm, may be due to close packing of grains in the initial stage of continuous film. During this stage of film growth, the thicker the film, the lower the density of defects in the film is. So the defected-related grain boundary diffusion occurs more difficultly. After this stage, the density of defects tends to be stable and the oxide layer gradually becomes thicker as the total effective thickness increases.

5. Conclusion

Copper thin films with nanometer-range thickness are prepared by electron beam evaporation. A new method, based on ellipsometry combined with transmittance iteration method, is used to obtain their effective optical constants, and thickness values. The mass thickness, effective thickness, and physical thickness are compared to evaluate different methods of measuring thin Cu film thickness. It is found that the effective thickness determined by this method is more close to physical thickness and has obvious difference from the mass thickness when the film is very thin. Thickness dependences of the surface microstructure and oxidation layer of thin copper film are analyzed. When Cu film is in the form of individual islands, the fraction of coverage is the most important factor influencing the effective optical constants; while in the stage of continuous film formation, the grain boundary diffusion process will play a major role.

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