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Native oxidation of ultra high purity Cu bulk and thin films

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Abstract

The effect of microstructure and purity on the native oxidation of Cu was studied by using angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and spectroscopic ellipsometry (SE). A high quality copper film prepared by ion beam deposition under a substrate bias voltage of −50 V (IBD Cu film at $V_s = -50$ V) showed an oxidation resistance as high as an ultra high purity copper (UHP Cu) bulk, whereas a Cu film deposited without substrate bias voltage (IBD Cu film at $V_s = 0$ V) showed lower oxidation resistance. The growth of Cu_2O layer on the UHP Cu bulk and both types of the films obeyed in principle a logarithmic rate law. However, the growth of oxide layer on the IBD Cu films at $V_s = 0$ and −50 V deviated upward from the logarithmic rate law after the exposure time of 320 and 800 h, respectively. The deviation from the logarithmic law is due to the formation of CuO on the Cu_2O layer after a critical time.

Keywords: Copper; Thin films; Oxidation; Thickness; Ion beam

1. Introduction

Copper has been extensively used as an interconnect material for ultra large-scale integration (ULSI) devices because of its low electrical resistivity and excellent electromigration resistance in comparison with those of aluminum and aluminum-based alloys [1]. The reliability of Cu interconnects is an important factor that determines the degradation of the device. However, native oxide layer formed on Cu surface is not self-protective and Cu itself is oxidized continuously in the air even at room temperature [2]. Since this oxidation rate is very slow at room temperature, the growth kinetics of native oxide layer on Cu bulk and Cu thin films has not been well understood so far.

At medium and high temperatures, many researchers have studied the oxidation kinetics of Cu [3–6]. The parabolic rate law was the most frequently observed above 300 °C. In contrast, at low temperatures below 300 °C, experimental data are quite sparse because of difficulty of precise measurements. Mott and Cabrera [7,8] have proposed theoretically the inverse logarithmic rate law and the cubic rate law for copper at low temperatures. However, experiment on room temperature oxidation of Cu has been rarely reported until now. Boggio [9] has investigated the behavior of oxidation of 6 N single crystal Cu at room temperature by using monochrome ellipsometry. The oxidation obeyed the logarithmic rate law, and the Cu oxide layer was composed of an inner layer of Cu_2O and an outer one of CuO, where the relative thickness between them depended on the oxygen partial pressure. However, Boggio did not characterize the oxide composition [9].

Using angle-resolved XPS, Suzuki et al. [2] have examined the native oxide layer formed at room temperature on the surface of ultra high purity iron which has been prepared by a combination of an ion exchange separation and zone refining technique [10], and investigated the native oxide layer on the surface of ultra high purity Cu prepared by the floating zone refining technique [11]. At the initial stage, the oxide layer formed on the iron surface was thicker than that formed on the Cu surface. With increasing oxidation time, the increase of the iron oxide layer was negligibly small, whereas the thickness of the Cu oxide increased with increasing the exposure time. In addition, they observed the formation of CuO on Cu_2O layer after a long exposure time, however, they did not make the oxidation kinetics clear [2].

In ULSI technology, it is very important to study the oxidation behavior of not only Cu bulk but also Cu thin films, because the Cu thin films are used actually as a wiring material in ULSI. O'Reilly et al. [12] have studied the oxidation

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behavior of Cu films in the temperature range from 50 to 150 °C using spectroscopic ellipsometry. Recently, Gao et al. [13] have found that the oxidation behavior of Cu films is different from that of Cu bulk in the temperature range from 175 to 400 °C. However, they have not examined the effect of the film quality and the oxidation rate law of the Cu films below 250 °C.

In our previous works [14–18], high quality Cu films have been successfully deposited from 6 N Cu target by an ion beam deposition (IBD) method with a negative substrate bias voltage. The IBD Cu film deposited at a negative bias voltage of −50 V (IBD Cu film at $V_s = -50$ V) showed an extremely fine and homogeneous morphology without columnar structure [14–17]. The FWHM value of the Cu(1 1 1) reflection peak has a minimum at the bias voltage of −50 V [15]. It corresponds to the minimum resistivity [15,17] as well as smooth surface and good morphology observed by SEM [14–16], FE-SEM [17] and atomic force microscopy [17]. According to glow discharge mass spectrometry (GDMS) [18], the purity of the IBD Cu film deposited at $V_s = -50$ V was 99.9968% which was higher than 99.9766% of the IBD Cu film deposited at $V_s = 0$ V. On the other hand, the purity of ultra high purity (UHP) Cu bulk was 99.9994% [18]. These values should be replaced by 99.9992%, 99.9989% and 99.9999%, respectively, if the contents of C, N and O are excluded, because the analysis of these gas elements by GDMS is often influenced by the interference from the residual gases in the vacuum system. The resistivity of the IBD Cu film at $V_s = -50$ V was very low and 18 ± 1 nΩm, which was close to 16.7 nΩm of UHP Cu bulk. On the other hand, the IBD Cu film at $V_s = 0$ V had a columnar structure with small grains less than 100 nm [15]. Consequently, the electrical resistivity of the IBD Cu film at $V_s = 0$ V was 99 nΩm [15,17].

The aim of the present work is to study the effect of the microstructure and the purity on the native oxidation of an UHP copper bulk and IBD Cu films at $V_s = 0$ and −50 V under ambient atmosphere. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is used for the non-destructive qualitative analysis of the native oxide layer in the range of a few nanometers. Spectroscopic ellipsometry (SE) is used to measure the thickness of the native oxide layer.

2. Experimental

Ultra high purity Cu bulk (UHP Cu) and IBD Cu films at $V_s = 0$ and −50 V were used as specimens. The UHP Cu was prepared by floating zone refining of 6 N Cu rod [19]. The residual resistivity ratio of the UHP Cu was as high as 22000. The UHP Cu rod was cold-rolled to a plate with thickness of 0.5 mm, and the plate was mechanically and electrochemically polished and followed by annealing in a dry hydrogen atmosphere for 24 h at 600 °C. The IBD Cu films were deposited on Si(100) substrate at the substrate bias voltages of 0 and −50 V under Ar pressure of 9 Pa using IBD system with 6 N Cu target [15].

Before exposing the specimen to the air, surface oxide layer on the specimen was removed by argon ion sputtering at 3 kV under the vacuum of 10^{-8} Pa. The exposure time of the samples for native oxidation was varied from 30 min to 1300 h.

The native oxide layer formed on the surface of each sample was characterized by angle-resolved X-ray photoelectron spectroscopy (ULVAC-PHI 5600). Al Kα X-ray source was used for the excitation of photoelectrons. Spectra were recorded in the energy range covering $Cu2p_{3/2}$, O1s and C1s peaks. To analyze Cu oxide layers, Cu $2p_{3/2}$ binding energy (metallic Cu: 932.6 eV, Cu_2O: 932.4 eV, CuO: 933.6 eV) and Cu LMM Auger transition binding energy (metallic Cu: 918.4 eV and Cu_2O: 916.5 eV) were used, because the chemical shift of Cu $2p_{3/2}$ XPS spectra was very small between metallic Cu and Cu_2O [20,21].

The CuO was characterized by high intensity shake-up satellites at about 9 eV higher binding energy than the main $2p_{3/2}$ and $2p_{1/2}$ peaks. Cu metal and Cu_2O could be distinguished from Cu LMM Auger spectra. The take-off angle θ between the direction of an analyzer and the specimen plane was varied in the range from 15° to 75° for the angle-resolved XPS measurements. The measured depth of the sample increased with increasing the angle θ.

Spectroscopic ellipsometer (JASCO M-211) was used to measure the thickness of the native oxide layer. In situ SE measurement was carried out in the range of wavelength between 350 and 850 nm at intervals of 1 nm using a Xe lamp as a light source. The incidence angle was fixed as 60° during the analysis. SE provides $\tan\Psi$ and $\cos\Delta$ spectra, where Ψ and Δ are the ellipsometric angles corresponding to the reflection of the polarized light.

In the determination of the thickness of the oxide layer, the optical single layer model consisting of only Cu_2O layer on Cu substrate was employed. Optical constants of layers were referred to the standard reference data [22]. The layers were assumed to be homogeneous and parallel-sided film. Fitting was performed between the measured spectral data and the optical model using a least-squares algorithm.

Since CuO layer is formed actually on Cu_2O layer after long time oxidation, we should consider the double layers model (CuO layer lies on Cu_2O layer, which are formed on the copper substrate). However, using the double layers model, it is difficult to obtain better-fit results because the optical constant of CuO is very close to that of Cu_2O. In addition, CuO layer formed on Cu_2O layer at low temperature is too thin to account to be one layer [20]. Therefore, single layer model is applied. As described later, the dependence of oxide layer thickness on the exposure time did not show any anomalous feature across the time at which CuO should be certainly formed. This means that the single layer model is enough to discuss the oxidation kinetics in the present experimental conditions.

3. Results and discussion

Fig. 1 shows the take-off angle dependence of AES spectra of the UHP Cu bulk, the IBD Cu films at $V_s = 0$ and −50 V exposed to the air at room temperature for 16 h. As shown in Fig. 1(a) and (b), AES spectra of the UHP Cu bulk and the IBD Cu film at $V_s = -50$ V show Cu_2O oxide peak at 916.5 eV and the metal peak at 918.4 eV only at higher θ (60° and 75°). This result means that these specimens have not been fully oxidized