Reduction of thin oxidized copper films using a hot-filament hydrogen radical source

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This article aims to provide practical information on the performance of a hot-filament radical source, with which it becomes feasible for metallization in ultralarge-scale integrated circuits, which has not been studied in detail thus far. A very simple arrangement using this technique allows the highly efficient generation of hydrogen radicals and a quick recovery of oxidized Cu surfaces to their original metallic state. The amount of CuO reduction was evaluated by measuring sheet resistance and also by transmission microscopy. The reduction started when the specimen temperature exceeded 100 °C, and several tens of nanometers Cu of film was formed without resulting in a serious increase in the specimen temperature. The amount of reduction was found to increase almost proportionately to the hydrogen radical flux. The Cu layer had a very flat surface topography showing no trace of self-agglomeration of Cu. The reduction of a thermally oxidized Cu specimen was also demonstrated. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2712197]

I. INTRODUCTION

Progress of miniaturization in integrated circuit (IC) manufacturing technology has been extremely indebted to the development of plasma processing, such as in dry etching, plasma chemical vapor deposition, sputter deposition, and sputter cleaning. The primary role of using plasma in microprocessing is to generate ions and radicals through inelastic collisions between neutral molecules and high-energy electrons. The generated ions are accelerated by an electric field towards the work so as to sputter its surface away. This is a purely physical process and provides the basis for sputter cleaning and deposition. Radicals are species having an unshared electron pair and are reactive enough to elicit a spontaneous chemical reaction. Chemical cleaning, etching, and deposition are typical and important applications of radical-based processing in micro- and nanoscale fabrication. Current advanced IC processing requires atomic-scale preciseness, thus, sputter-based cleaning procedures are becoming less favored. Electrical damage induced by charged species has also been of serious concern. In addition, plasma processing is generally unaffordable due to the cost of equipment outlay and ownership.

The hot-filament radical source has been proposed as an alternative. A hot filament is a refractory metal wire that is electrically heated to usually above 1800 °C. At its surface, the dissociation of molecules is catalytically promoted so as to generate short-lifetime radicals. This is a purely pyrolytic process and, thus, is beneficial in preventing charge-up damage and bombardment by energetic ions and electrons. The hot-filament technique became very popular in microprocessing in the 1980's especially for molecular beam epitaxy[1] and for diamond chemical vapor deposition.[2] The application of the hot-filament technology to Si or large-scale integrated circuit (LSI) processing has been proposed as a beneficial alternative to plasma technology.[3]

This article demonstrates the use of a hot-filament radical source to perform soft and neutral recovering of oxidized Cu surfaces. The oxidation of a Cu surface by exposure to the atmospheric environment is a serious issue concerning the metallization in LSI processing. For instance, via bottoms or bonding pads of LSI, Cu interconnects suffer such deterioration, and insufficient removal or cleaning of the deteriorated surface may easily cause interconnect failures.[4] Dry chemical cleaning with hydrogen atoms (radicals) are known to efficiently remove the surface oxides/contaminants;[4,5] however, using a plasma radical source does not have a significant edge as stated above.

The reduction of Cu oxides with a hot-filament radical source has been reported;[6,7] however, practical information such as the effect of process parameters on the reduction thickness seemed not well documented. Such information is practically crucial to assess process adaptability of the hot-filament technology. In the present work, we focused on studying the hot-filament technique with respect to (1) the dependence of reduction amount on process parameters such as filament temperature and (2) the characterization of processed films.

II. EXPERIMENT

Figure 1 shows an experimental arrangement used in this work. The filament used was a straight tungsten wire, 0.5 mm in diameter. The filament was electrically heated at

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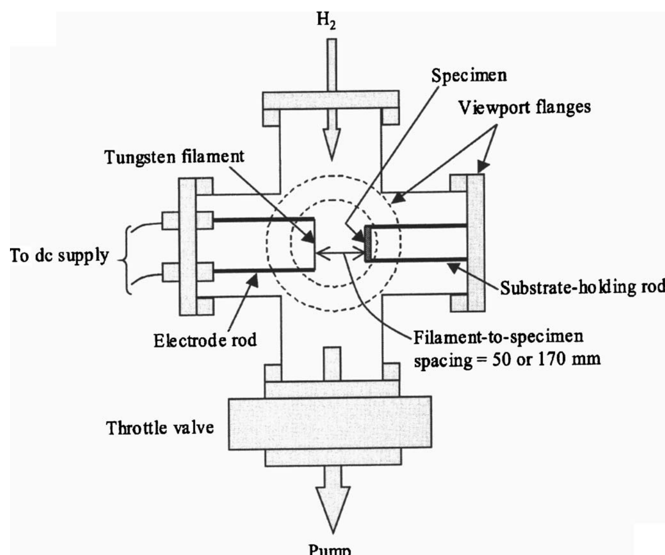

FIG. 1. Schematic diagram of the apparatus used in this work.

1500–2500 °C in a hydrogen ambient. The ambient pressure was varied from 1×10^{-5} to 100 mTorr $(1.3\times10^{-3}-13$ Pa). The temperature of the filament was set to a target value by adjusting the filament current.

Hydrogen gas was admitted at the top of the vacuum chamber at a typical flow rate of 30 SCCM (SCCM denotes cubic centimeter per minute at STP) using a mass-flow controller. The reactor pressure was adjusted with an automatically controlled throttle valve (VAT type F64) placed between the chamber and a high compression turbo molecular pump (Shimadzu TMP-1103, 800 L/s for H_2). The chamber pressure was measured with a Tylan CDLD 01S06 pressure transducer.

A specimen was placed in front of the filament, 50 or 170 mm apart. Sputtered CuO films 5000 Å in thickness were used as specimens and in addition to running a thermally oxidized Cu films in another case. The specimen size was approximately 25×25 mm^2. The specimen was mechanically clamped at its two opposite edges to stainless-steel rods. No pedestal or substrate heater was employed; therefore the specimen was heated only by heat radiation from the filament. The specimen temperature was monitored at the backside by using a very thin (200 μm in diameter) thermocouple. The thermocouple was placed in a small hole drilled to half the depth of the wafer thickness and was fixed using molding cement or vac seal™. The surface temperature was also evaluated using temperature sensitive paint. The variance from the thermocouple measurements was less than 10 °C. The temperature of the filament was measured with a disappearing filament optical pyrometer without emissivity correction.

For some experiments a quadrapole mass spectrometer (QMS), specially tuned for low m/e measurement (MKS-Spectra MicroVision), was used to perform qualitative evaluation of H radical intensity. The QMS was mounted on a flange in place of the one for specimen fixing. The sheet resistance of the specimen was measured with a four-terminal probe. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were used for characterizing the treated films.

TABLE I. Pyrometer temperature and $m/e=1$ ion current as a function of filament current. H_2 pressure of 10 mTorr (1.3 Pa) and filament diameter of 0.5 mm.

Filament current (A)	Pyrometer temperature (°C)	$m/e=1$ current (nA)[a]
0	⋯	3.8
5	1120	n/a
7.5	1380	n/a
10	1650	3.8
12.5	2000	4.0
15	2250	4.0
17.5	2500	4.1

[a] $m/e=2$ current was about two orders of magnitude larger (e.g., 0.28 μA at 10 mTorr). Ionization energy was 70 eV.

III. RESULTS AND DISCUSSION

A. Simple verification of H radical generation and CuO reduction

Before going into the details, we demonstrate here the basic performance of our equipment as a tool for CuO reduction. Table I shows how the filament temperature and H radical concentration increased with filament current, here the amount of H radical was estimated as $m/e=1$ current of QMS ($m/e\equiv$mass/charge ratio). The ionization energy used for this measurement was 70 eV. The filament temperature increased almost linearly in this range, and an increase in the $m/e=1$ current was observed above around 1800 °C. This trend agrees well with past researches focused on H radical generation from hot filament.[8,9]

The occurrence of CuO reduction also evidences the generation of H radicals. After short exposure to the hot-filament radical source, sputtered CuO films, originally very dark brown, showed a shiny copper color. Conversely, anealing of CuO film under the same H_2 ambient, but at a much higher temperature of 450 °C, did not result in a change of color.

These results well demonstrate the generation of H radicals at the hot filament and the reduction of CuO by these radicals. The CuO reductive behavior is of course the subject of this article and the details are described hereforth.

B. Reductive behavior of sputtered copper oxide

1. Change of sheet resistance and effect of specimen temperature

Figure 2 shows changes of the sheet resistance with process time for the filament substrate at spacings of 50 and 170 mm. The process conditions were the filament temperature of 2250 °C and the H_2 ambient pressure of 10 mTorr (1.3 Pa). It was observed that the sheet resistance had rapidly decreased with time elapsed and then leveled off. The rate of decrease became remarkably large when the filament-substrate spacing L was decreased to 50 mm, and a lower sheet resistance value was achieved.

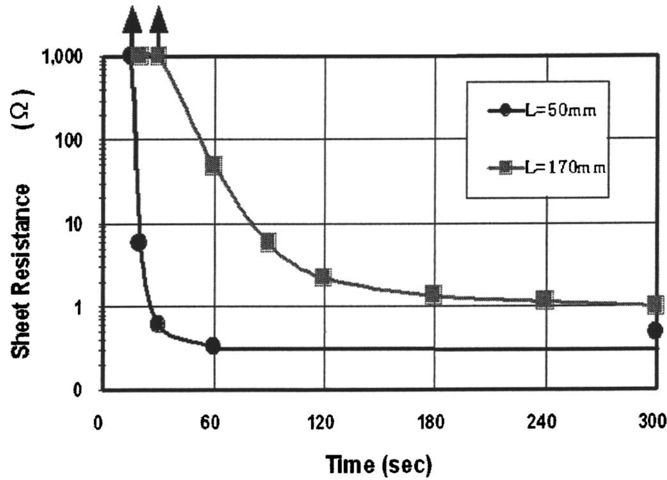

FIG. 2. Change of sheet resistance of CuO films with process time.

The thickness of the reduced Cu layer was calculated from the data in Fig. 2 and is plotted in Fig. 3. We assumed a Cu resistivity of 2.0 $\mu\Omega$ cm in the calculation as a typical value of dry-processed Cu thin films. Note that this value is slightly higher than the bulk value (1.6 $\mu\Omega$ cm). The maximum thicknesses were approximately 60 and 20 nm for $L=50$ mm and $L=170$ mm, respectively. The Cu thicknesses determined with cross-sectional transmission microscopy (XTEM) agreed well with these estimated values, indicating that the above assumption is reasonable. The XTEM photos were shown and dicussed later.

In Fig. 3, the change of substrate temperature during the process is superimposed using dashed lines. Each dashed line contours the temperature reached in a given process time for

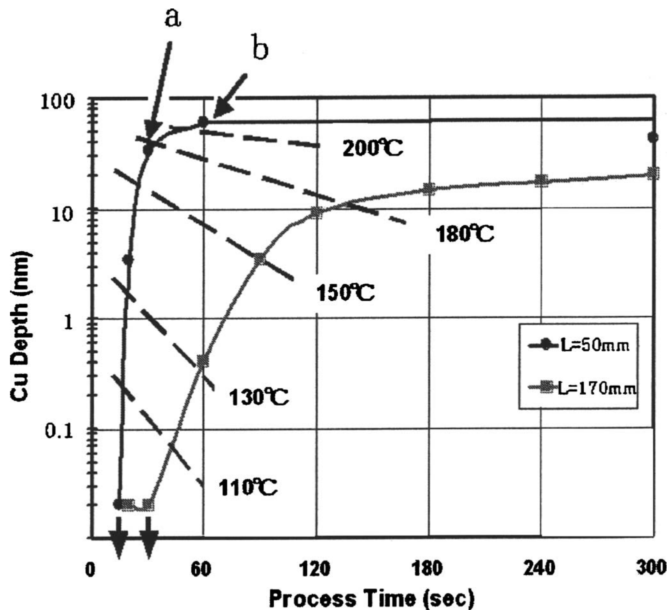

FIG. 3. Estimated thickness of CuO-reduced Cu layer for $L=50$ and 170 mm. The dashed line contours the temperature reached in a given process time for the two different values of filament-to-specimen spacing. Data labeled a and b refer to XTEM specimens shown in Fig. 6.

the two different values of filament-to-specimen spacing. For instance, for the line labeled 130 °C, the substrate temperature increased to 130 °C in about 20 s when $L=50$ mm, but a longer time of about 60 s was needed when L was increased to 170 mm. From these figures, it is easily understood that the reduction of CuO starts at above 100 °C and proceeds remarkably at 130–150 °C.

The reduction of CuO by H_2 molecules, $CuO+H_2 \rightarrow Cu + H_2O$, is generally a high temperature process.[10] The elementary reactions of this reaction can be written as

$$H_2 \rightarrow 2H, \quad (1)$$

$$CuO + 2H \rightarrow Cu + H_2O. \quad (2)$$

As for the direct reduction of CuO by H_2, reaction (1) can be the rate-determining step. However, in our experiments, reaction (1) itself is no longer involved as a reduction mechanism, because H atoms are generated at the high temperature filament surface and are supplied towards the CuO surface. Another possible process that is related to reaction (1) is the transportation of H towards the CuO surface. This process can dominate the reduction process when reaction (2) is sufficiently fast.

Possible processes that can limit reaction (2) are (1) the diffusion of a reducing agent, in our case H, through the reduced Cu layer, (2) the desorption of H_2O, and (3) reaction (2) itself, by ignoring further possible elementary processes in which Cu_2O is involved. When the diffusion of H is the rate-limiting process, the reduction reaction is expected to follow a well-known parabolic theory, where the reduction thickness increases proportionally to the square root of the process time (and also to the square root of H density at the surface). It has been reported indeed that the reduction of Cu oxide by hydrogen plasma proceeds in this manner.[5] The desorption of H_2O from H-reduced Cu oxides is a high-temperature reaction and does not take place at least at 400–510 K.[6] It was also reported that the reduction of oxidized metal surfaces by hydrogen radicals proceeds almost spontenously without having a large activation energy;[11] therefore, reaction (2) itself is speculated not to be the rate-limiting step.

After excluding H_2O desorption and reaction (2) itself, two processes still remain as rate-limiting candidates, namely, the supply of H to the surface from the filament and the diffusion of H through the growing Cu. At the beginning of reduction the former is speculated to be rate limiting from the following estimation. The initial reduction rate calculated from the Cu thickness is approximately in the order of 10^{21} m^{-2}/s^{-1} (40 nm for 10 s). The diffusion coefficient of H in Cu at 400–500 K is in the order of 10^{-11} m^2/s.[12] Using this value, the concentration gradient of H is estimated at 10^{32} m^{-4}. Simply assuming that the H concentration at the Cu/Cu oxide interface is zero, the volumetric concentration of H at the surface side of Cu layer is 10^{24} m^{-3}. This value is slightly lower than the maximum H density in Cu, or the solubility of H. This estimation suggests that the flux of H to the surface limits the initial reduction rate. These two pro-

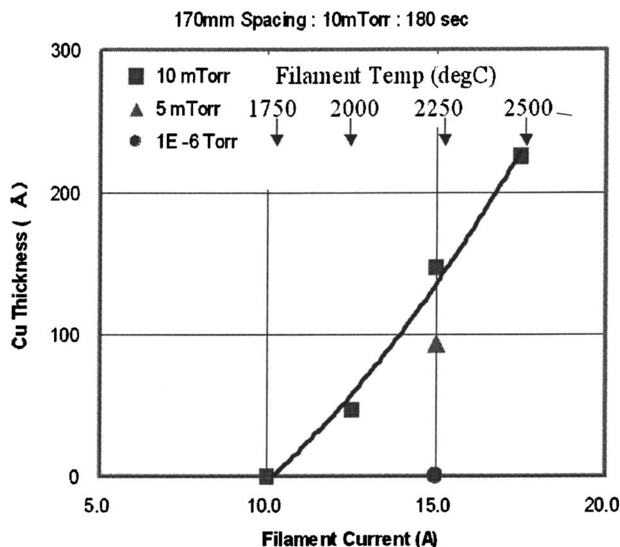

FIG. 4. Effects of filament temperature and hydrogen pressure on Cu thickness for $L=170$ mm.

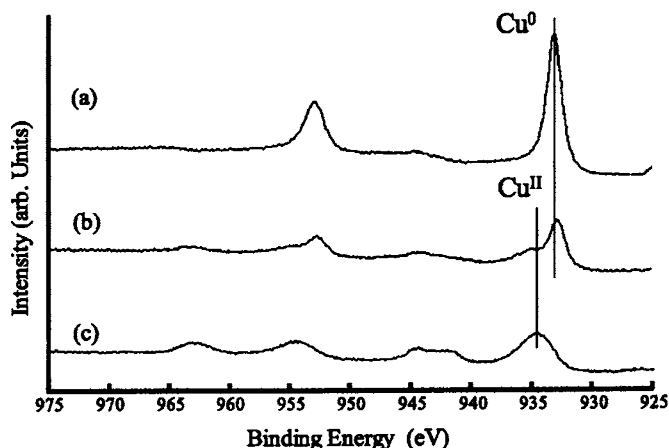

FIG. 5. XPS spectra of processed and unprocessed CuO films.

cesses will compete where the former proceeds fast at the begining of reduction and the latter becomes dominant as the Cu thickens.

2. Effects of filament temperature, ambient pressure, and filament-to-specimen distance

Figure 4 shows the Cu thickness plotted against the filament current and temperature. The degree of reduction, here the Cu thickness, increased with filament current, or filament temperature. Reduction starts at a filament temperature of about 1800 °C, which agrees well with the data shown in Table I as well as past research on the catalytic pyrolysis of H_2 using heated refractory metals.[8,9] This suggests that the reduction rate is determined by the incident flux of H atoms as far as the other operational parameters, such as substrate-filament spacing, substrate temperature, and filament temperature, remain unchanged.

When the H_2 pressure was halved, the reduction thickness was decreased by approximately 40%. By reducing the pressure by 50%, the number of molecules that strike the specimen surface, of course, decreases by 50%. That is, the obtained reduction thickness was 10% less sensitive to the pressure. This can be explained by employing simple gas-kinetics discussion. The recombination reaction of hydrogen atoms is a three-body collision, thus, it is largely pressure dependent.[13] Under our experimental condition of 10 mTorr, the mean free path of a molecule is in the order of 1 cm (300 K), small enough to induce collisions during travel from the filament to the specimen. When the pressure is reduced by 50%, the recombination rate is reduced to $(0.5)^3$ or 13%, and the probability of survival of H atoms becomes $\exp(0.13)=1.13$ times larger. Therefore, the flux of H atoms incident to the specimen surface becomes $0.5\times 1.13=0.57$ or approximately 60%, which is in fair agreement with our observation. It is concluded again that the amount of CuO reduction is determined by the intensity of H flux.

The effect of the filament-to-substrate distance L can be discussed in the same way. Our filament was a linear wire and was arranged parallel to the specimen. The amount of H flux at the specimen position is basically inversely proportionate to L, in this case $170/50\approx 3$. By taking into account a decrease in recombination probability due to decreasing L, the estimated amount of H flux should be increased by ten times. This is, in fact, in agreement with the results in Fig. 2. For instance, at about 130 °C, the reduction rates for $L=50$ mm and $L=170$ mm are estimated at approximately 0.2 and 0.03 nm/s, respectively, giving the ratio of 8. When discussing the effect of L, the effect of heat flux should also be taken into account. Indeed, when L was increased, the substrate temperature was decreased by approximately several tens of degrees (see Fig. 3). This temperature decrease corresponds to the decrease in the H diffusion coefficient to 1/3–1/4 and thus to the decrease of the reduced Cu thickness.

C. Characterization of CuO-reduced Cu

Figure 5 shows the XPS spectra obtained from processed and unprocessed CuO films. The as-received film (spectrum c) shows Cu^{II} and associated peaks. The surface that was exposed to the atmosphere after the H-radical exposure showed a Cu^0 signal of 933 eV as well as the Cu^{II} peak (spectrum b). After surface etching with an Ar ion beam in the XPS apparatus, the Cu^0 peak became remarkably present and practically no presence of Cu^{II} peak was confirmed (spectrum a). This clearly indicates that the surface was reduced to metallic Cu.

Figure 6(a) shows an XTEM image of a CuO film processed under the conditions of $L=50$ mm and 30 s at 10 mTorr. The reduced Cu, having a darker contrast against the underlying columnar CuO layer, shows a continuous layer structure that consists of connected grains approximately 20 nm in diameter. Small voids underneath Cu and the adjacent CuO part can be seen exhibiting a slightly different contrast against the bulk CuO layer. The thickness of the Cu layer is approximately 20 nm and is almost the same as the grain size. This value fairly agrees with the electrically

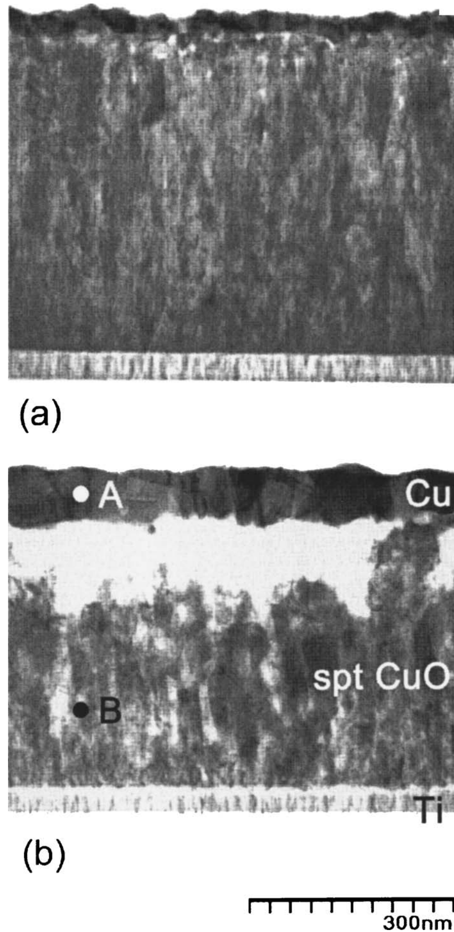

FIG. 6. XTEM image of CuO films processed for a fixed spacing $L=50$ and for 30 s (a) and 60 s (b). The ambient pressure was 10 mTorr.

determined thickness as shown in Fig. 2, which indicates that the resistivity (2.0 $\mu\Omega$ cm) assumed in the Cu thickness evaluation, was appropriate. Note that each layer was identified qualitatively by using energy dispersion X-ray spectroscopy (Fig. 7).

The specimen processed for 60 s has a larger Cu thickness of approximately 60 nm [Fig. 6(b)]. The grain structure of the Cu layer is more developed, and again, the grain size seems to be almost the same as the Cu thickness. The void between Cu and CuO grows remarkably, resulting in the structural discontinuity between the two layers.

Although the void formation itself is somehow granted, the CuO-reduced Cu does not have to take on a flat topography like in Figs. 6(a) and 6(b). As stated above, the agglomeration of Cu or the formation of a spongelike structure is a more natural phenomenon to be expected, because Cu has a high surface energy. Agglomeration can take place only when the surface Cu atoms move around freely by acquiring high thermal energy. From this basis, in our experiments, the surface temperature did not seem to reach high enough to allow Cu atoms to migrate freely but high enough to allow grain growth with keeping a smooth surface topography.

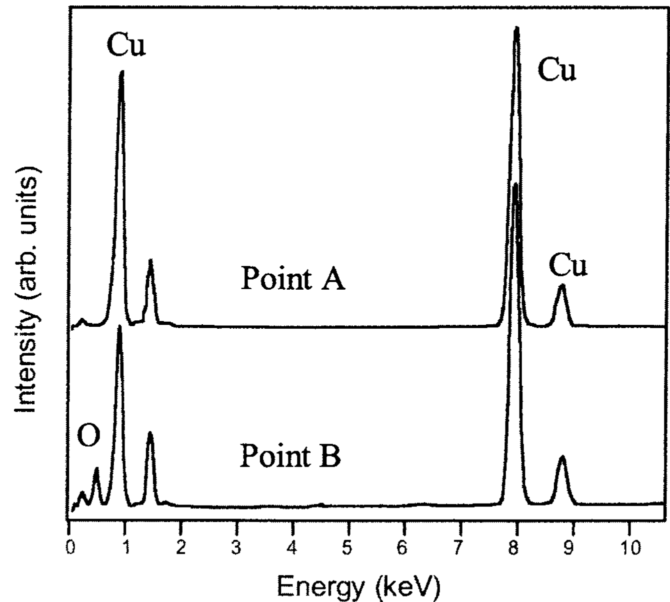

FIG. 7. Energy-dispersion X-ray spectra of CuO film taken at points A and B of Fig. 6(b).

D. Reduction of thermally oxidized Cu

Finally, the hot-filament radical source was employed to recover a thermally oxidized Cu surface, and the results are briefly described here. A 1 μm thick sputtered Cu film was oxidized at 150 °C in the atmosphere with a laboratory hot plate. The sheet resistance of this film was about 60 kΩ. After the H-radical irradiation, the sheet resistance was reduced to 1.8 Ω. Figure 8 shows the XPS depth profiling of the oxidized and treated Cu films. It is obvious that the treated film shows practically no trace of oxygen. This result demonstrates that our hot-filament technique can be employed to recover oxidized Cu surfaces.

IV. CONCLUSIONS

This article demonstrated the capability of using a hot-filament hydrogen radical source for recovering oxidized Cu surfaces. We mainly employed sputtered CuO to study its reduction to Cu. The formation of hydrogen radicals was found to proceed significantly when the filament was heated above approximately 1800 °C. The reduction of CuO was confirmed with XPS and other instrumental techniques. The

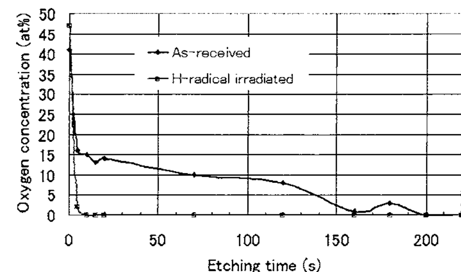

FIG. 8. XPS depth profiling of thermally oxidized and H-radical-irradiated Cu films.

amount of CuO reduction was evaluated from film sheet resistance measurements, and apparent Cu thicknesses were determined from the measured sheet resistance values. The electrical thickness measurement was validated by our direct observation with XTEM. The degree of reduction was also found to increase almost proportionately to the hydrogen radical flux. The saturation of Cu thickness over time elapsed was observed to occur. The CuO-reduced Cu layer had a very flat surface topography without showing self-agglomeration. The surface of thermally oxidized Cu can be recovered as metallic Cu. In summary, using the hot-filament radical source is practical and affordable technology in Cu metallization to recover oxidized Cu surfaces to flat and high quality Cu.

ACKNOWLEDGMENTS

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