Barrier Properties of an Electroless Deposit of Co-W-P Alloy

Sho Kanzaki, Toshiaki Shibata, Seigo Kurosaka, Yukinori Oda,
and Shigeo Hashimoto
C.Uyemura & Co.,Ltd. Hirakata, Osaka 573, Japan

***Abstract*— It is well-established that a Co alloy deposit has high electromigration resistance and thermal diffusion resistance to Cu. We prepared an electroless deposit of Co-W-P with different W contents on the Cu substrate by changing the Co-W-P bath parameters. After heat treatment at 200-400°C with air or N_2 atmosphere, Cu diffusion to the surface was measured. A Co-W-P layer has excellent barrier properties for Cu in N_2 heat treatment. However, Cu diffused to the surface when the entire Co-W-P (W=0 and 11wt.%) layer was oxidized at high temperature in ambient air.**

The results indicate that the oxidized layer of Co-W-P has no barrier effect for Cu. In the Co-W-P deposit with high W content (W=23wt.%), an unoxidized layer remained and only a small amount of Cu was detected on the surface. We confirmed that Co-W-P (W=23wt.%) was difficult to oxidize and Cu diffusion was suppressed by preventing oxidization of the Co-W-P deposit.

Keywords—Electroless deposit, Tungsten content of Co-W-P, Copper diffusion, Oxidation layer, XPS

I. Introduction

Recently, semiconductor devices have been required to advance to high-speed and high-performance with miniaturization of wirings, low resistivity and low-K dielectric properties. With further wiring miniaturization, it becomes difficult to use conventional sputtering for the barrier and seed layers. Therefore these are studied by the electroless deposition process [1]. It is known that the Co alloy deposit has a barrier property in the Cu wiring, and in particular, the good electromigration resistance in the Cu wiring has been reported with the electroless deposit of Co-W-P [2-5].

In this study, we investigated Cu diffusion in the various W contents of Co-W-P deposits, the condition of heat treatment temperature and atmosphere. We revealed that higher W content within Co-W-P deposits improved barrier properties for Cu diffusion.

II. Experimental Proceduree

A. Preparation methods of test coupons

The substrates were C1100P (Japanese Industrial Standard (JIS)) to which 10 μm thick electrolytic copper was plated. Each coupon was plated with electroless Co-W-P by using plating chemicals commercially available from C.Uyemura & Co., Ltd. The plating process is shown in TABLE I.

Coupons of Co-W-P deposits were plated by changing the make-up volume, and the W content ratio of these coupons was adjusted to 0, 3.5, 6, 11, 17 and 23 wt.% with 0.1μm thickness.

TABLE I. Plating Process

Process	Time
Conditioner	3 min
Etching	1 min
Acid rinse	1 min
Pre-dip	0.5 min
Activator	2 min
EL-Co	Target thickness 0.1 μm

B. Evaluation method

Each plated coupon was exposed to air and N_2 atmospheres at 200, 280, 350 and 400°C for one hour. For the instruments, a muffle furnace (Yamato Science, FM 38) and a vacuum reflow oven (Unitemp, VSS-450-300-EP) were used.

Following heat treatment, surface and depth profile analyses were performed using an X-ray photoelectron spectrometer (XPS, ULVAC-PHI, Quantera II).

The surface and cross-section of Co-W-P deposits were evaluated using a field emission scanning electron microscope (FE-SEM, Zeiss, ULTRA 55) and a focused ion beam (FIB, Hitachi High-Technologies, XVision 210 DB).

III. Result and Discussion

A. Cu concentration of the Co-W-P deposit surface

First, the W content ratio of the Co-W-P coupons was prepared at 0, 3.5, 6 and 11 wt.%. Each coupon was exposed with and without heat treatment to the air atmosphere.

The diffused Cu concentration (at.%) on the surface was analyzed by XPS. (X-ray Photoelectron Spectroscopy, aka Electron Spectroscopy for Chemical Analysis-ESCA). The results are shown in TABLE II.

In all coupons, Cu was detected on the surface in the heat treated condition over 350°C. At 280°C, Cu was detected in 0, 3.5 and 6 wt.% coupons. Cu was not detected in the 11 wt.% coupon. From this, it was suggested that the high W content of Co-W-P deposit suppressed the Cu diffusion.

To confirm the higher W content of the Co-W-P deposit, we investigated the Co-W-P bath condition.

TABLE II. Cu concentration on the surface by XPS analysis (Air, 200-400°C-1 h) (at.%)

Heat treatment atmosphere	Heat treatment temperature	W content (wt.%)			
		0	3.5	6	11
as-plate		0.0	0.0	0.0	0.0
Air	200 °C	0.0	0.0	0.0	0.0
	280 °C	0.4	0.1	0.1	0.0
	350 °C	7.2	5.7	5.5	5.9
	400 °C	40.8	No data	No data	57.0

B. Investigation of higher W content ratio of Co-W-P deposits

Fig. 1 shows the co-relation of W content ratio of the Co-W-P deposit with the WO_4^{2-} and $H_2PO_2^-$ concentration of the electroless Co bath. When the WO_4^{2-} concentration was higher, the W content ratio was saturated. On the other hand, when $H_2PO_2^-$ concentration was 40%, the W content ratio increased by approximately 1.8 times. Equations (1), (2), (3) and (4) show the oxidation reaction of $H_2PO_2^-$, the reduction reaction of Co^{2+}, the reduction reaction of $H_2PO_2^-$, and the reduction reaction of WO_4^{2-}.

$$H_2PO_2^- + 3OH^- \rightarrow HPO_3^{2-} + 2H_2O + 2e^- \quad (1)$$

$$Co^{2+} + H_2PO_2^- + 3OH^- \rightarrow Co + HPO_3^{2-} + 2H_2O \quad (2)$$

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (3)$$

$$WO_4^{2-} + 8H^+ \rightarrow W + 4H_2O \quad (4)$$

When $H_2PO_2^-$ is oxidized, it releases electrons. By receiving this electron, Co^{2+} ion is reduced and metalized. Along with this, a reduction reaction of $H_2PO_2^-$ and WO_4^{2-} ion occurs, and P and W are co-deposited into the Co deposit.

As the $H_2PO_2^-$ concentration moves lower, the W content becomes higher (Fig.1). Therefore it is suggested that reduction reactions of $H_2PO_2^-$ and WO_4^{2-} ion are competitive reactions, and the W content of Co-W-P deposit increases by reducing the supply source of P. Based on these considerations, the coupons of W=17 and 23 wt.% could be prepared by adjusting the bath concentration of both WO_4^{2-} and $H_2PO_2^-$ ion.

TABLE III shows the relationship between the W content of the Co-W-P deposit and concentrations of WO_4^{2-} and $H_2PO_2^-$ ions.

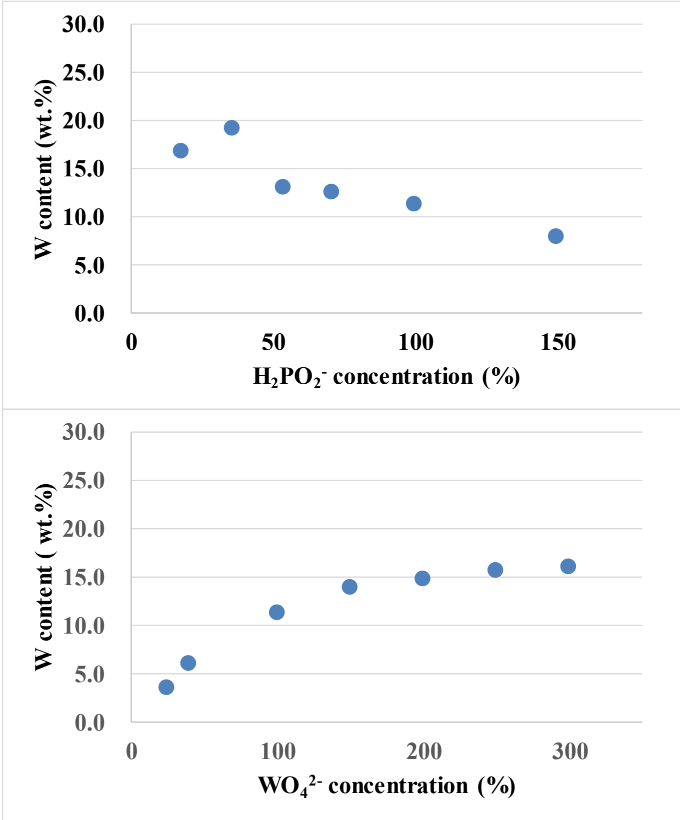

Fig. 1 W content of Co-W-P deposit (upper part: case of changing $H_2PO_2^-$ concentration, lower part: case of changing WO_4^{2-} concentration)

TABLE III.

TABLE IV. Result of the relation between W content of Co-W-P deposit and the concentration of both WO_4^{2-} and $H_2PO_2^-$ ion

	W content (wt.%)			
	0	11	17	23
WO_4^{2-} concentration (%)	0	100	200	200
$H_2PO_2^-$ concentration (%)	100	100	72	36

C. Observation of Co-W-P deposit

Fig. 2 shows the images of FE-SEM and FIB cross-section of the Co-W-P deposit of 0, 11 and 23 wt.% as W content. The crystal morphology changes as the W content ratio rises.

D. Cu diffusion barrier property of higher W content ratio of Co-W-P deposit

TABLE V is the result of Cu concentration on the Co-W-P surface in the relation between W content of Co-W-P deposit and the heat treating temperature. Cu was detected on the surface at 400°C air atmosphere. However, at 350°C, only a small amount of Cu was detected in the W=23 wt.% coupon, compared with lower W content coupons.

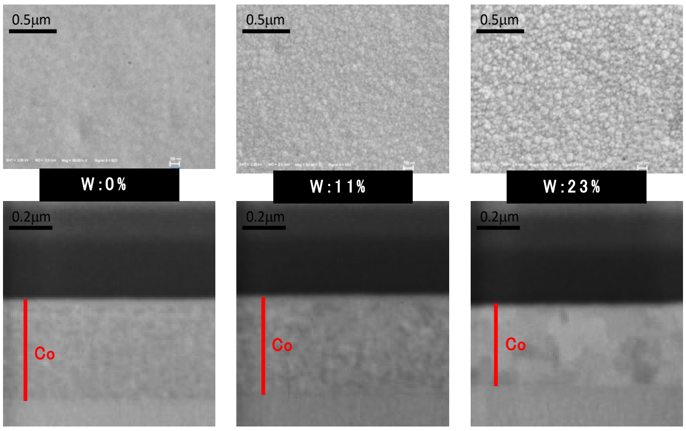

Fig. 2 FE-SEM (upper part) and FIB observation image (lower part) (Co-W-P deposit thickness: about 0.5 µm)

TABLE V. Cu concentration on the surface by XPS analysis (Air and N_2, 200-400°C-1 h) (at.%)

Heat treatment atmosphere	Heat treatment temperature	W content (wt.%)			
		0	11	17	23
as-plate		0.0	0.0	0.0	0.0
Air	200 °C	0.0	0.0	0.0	0.0
	280 °C	0.4	0.0	0.0	0.0
	350 °C	7.2	5.9	1.1	0.3
	400 °C	40.8	57.0	No data	54.6
N_2	400 °C	0.0	0.0	0.0	0.0

When N_2 heat treatment was performed at 400°C, Cu was not detected in any coupon.

Fig. 3 is the XPS result of Cu concentration on the surface of Co-W-P deposit with W=0, 11 and 23 wt.% following heat treatment at 400°C in an air atmosphere. In the W=23 wt.% coupons, Cu was not detected until the 30-minute point.

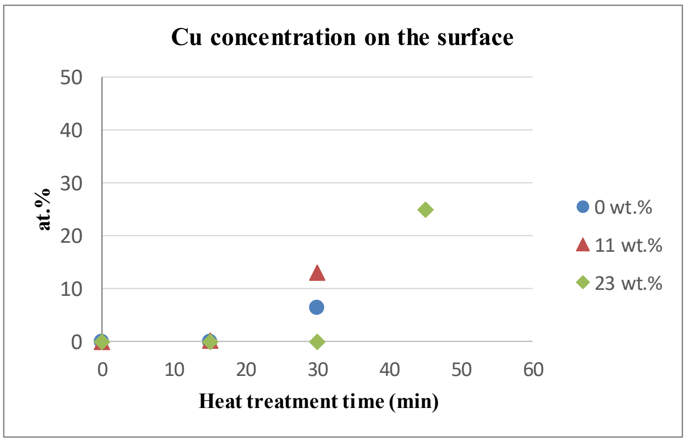

Fig. 3 Cu concentration on the surface by XPS analysis (Air, 400°C) (at.%)

On the other hand, in the W=0 and 11 wt.% coupons, Cu was detected with 30 minutes exposure. This finding suggests that higher W content suppresses Cu diffusion.

Fig. 4 shows an XPS depth profile of W=0, 11 and 23 wt.% with coupons as-plated ((a)-(c)) and heat treatment at 350°C in an air ((d)-(f)) or N_2 atmosphere ((g)-(i)).

For as-plated coupons (Fig. 4 (a)-(c)) and those heat treated in an N_2 atmosphere (Fig. 4 (g)-(i)), the XPS profiles were very similar: no oxygen was detected in the Co-W-P layer. In coupons heat treated in an air atmosphere (Fig. 4 (d)-(f)), oxygen was detected in the Co-W-P layer. The entire range of deposits, from 0 to 11% W was oxidized. However in the W=23 wt.% deposit, oxygen was detected until a depth of 100nm, and an unoxidized layer remained.

This reveals that higher W content in a Co-W-P deposit suppresses oxidation in an air atmosphere; also, an unoxidized layer of Co-W-P has excellent barrier properties for Cu.

E. *Mechanism of Cu diffusion*

Fig. 5 shows the model of the occurrence of Cu diffusion. With heat treatment in an N_2 atmosphere, no Cu diffused on the surface in either the low W content (Fig. 5 (a)) or high W content (Fig. 5 (b)) coupons. This is because the Co layer is not oxidized.

With heat treatment in an air atmosphere, Cu diffused to the surface in the low W content (Fig. 5 (c)) coupon, but not the high W content (Fig. 5 (d)). This is because the latter suppresses oxidation, leaving an unoxidized layer.

IV. Conclusions

A Co-W-P layer provides high barrier properties for Cu diffusion. When Co is oxidized, however, the barrier properties diminish.

A higher W content in a Co-W-P deposit suppresses oxidation in an air atmosphere; an unoxidized layer of Co-W-P has excellent barrier properties for Cu.

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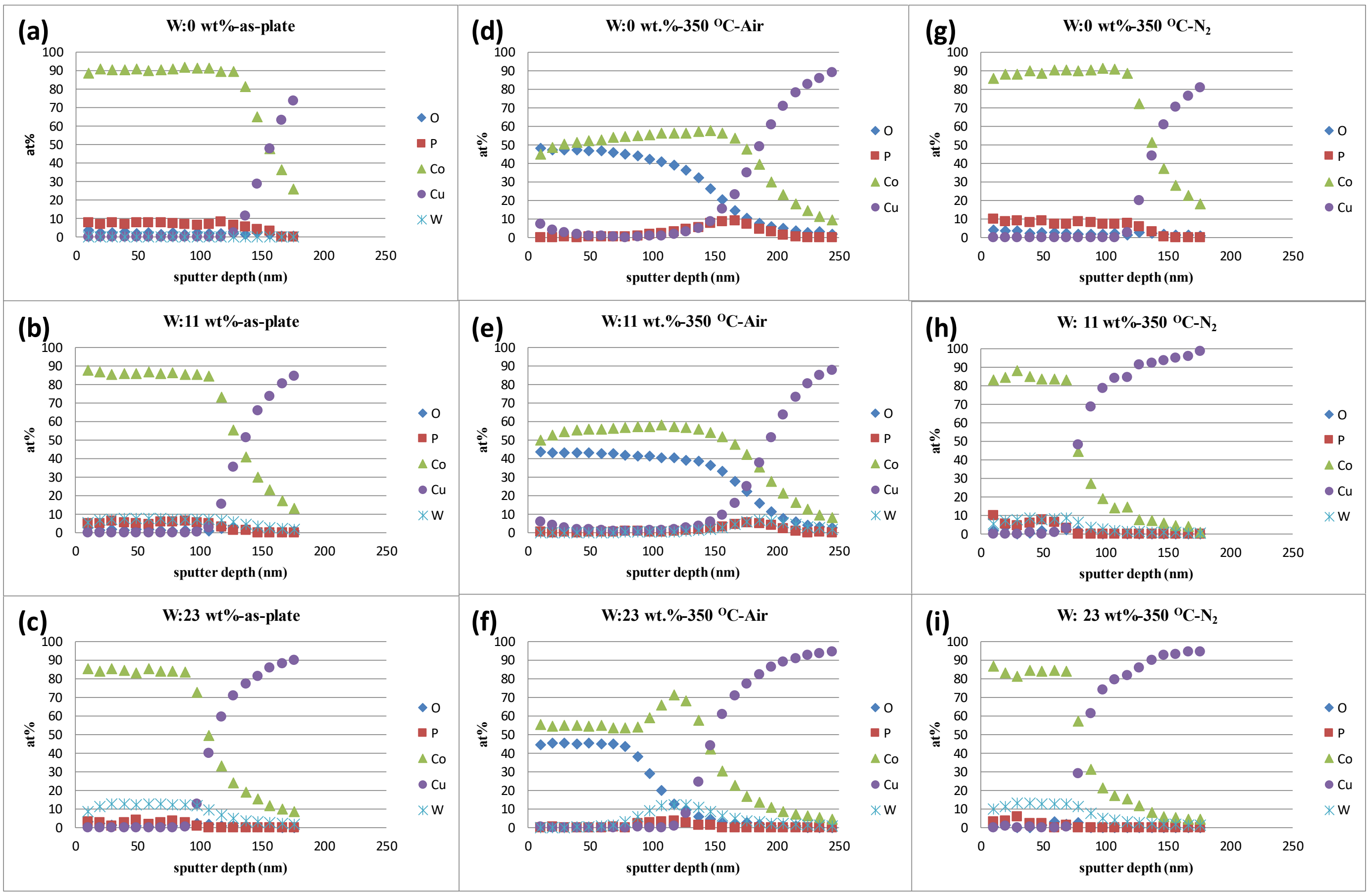

Fig. 4 XPS depth profile ((a)~(c) : as-plate, (d)~(f) : Air, 350°C-1h, (g)~(i) : N_2, 350°C-1h)

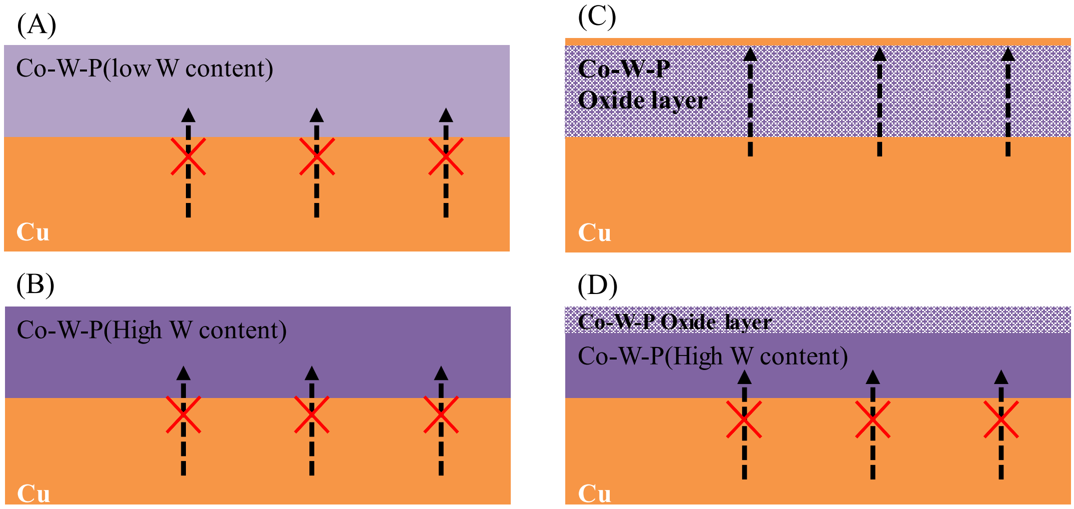

Fig. 5 Model of Cu diffusion occurrence (Heat treatment in N_2 : (A), (B), Air : (C), (D))