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Characteristics of electrodeposited CoWP capping layers using alkali-metal-free precursors

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Abstract−CoWP films, used as a capping layer for a copper interconnection, were electrodeposited using alkali-metal-free precursors, and the effect of the electrolyte concentration on the film characteristics such as the thickness, composition, and microstructure was investigated. The current density and the film thickness increased with the concentration of cobalt, tungsten, and phosphorous precursors. When the cobalt ion concentration in the electrolyte was increased from 0.01 to 0.09 M, the cobalt content in the film increased from 67 to 89 at%, while the tungsten and phosphorous contents decreased from 16 to 0.7 and 17 to 10 at%, respectively. The tungsten and phosphorous contents also increased as their corresponding concentrations increased in the electrolyte. Microstructural analyses showed that the tungsten and phosphorous content in the film greatly affected the crystallinity of the CoWP films electrodeposited using alkali-metal-free precursors.

Key words: CoWP Films, Capping Layer, Copper Interconnection, Electrodeposition, Alkali-metal-free Precursors

INTRODUCTION

The use of copper as an interconnection material is increasingly needed in the fabrication of microelectronic devices because of its higher electrical conductivity and better electromigration resistance than aluminum [1,2]. Copper, however, is easily oxidized and rapidly diffuses into silicon or oxide films, resulting in the abnormal operation of these devices [3,4]. To suppress copper oxidation and diffusion, capping/barrier layers have been deposited on the surface of copper.

The use of iron group metals (Fe, Co, Ni) as capping/barrier materials for copper interconnection has drawn much attention because of their good oxidation and diffusion resistances as well as their stability at high temperatures. However, films deposited from iron group metals alone have many grain boundaries, which provides diffusion pathways for copper. It is known that the grain boundaries of the iron group metal films can be stuffed with refractory metals and phosphorous (or boron) [5,6]. Hence, a refractory metal and phosphorous (or boron) are usually deposited together along with the iron group metals.

Various metallic films have been proposed as capping/barrier layers, including NiReP [7], CoWP [8-13], CoWB [14], NiWB [15], NiCoP [16], CoMoP [17], and so on. These films were formed by using wet chemical methods such as electroless and electro plating. In most plating baths, alkali-metal-containing precursors have been used. However, in the bath, alkali-metal ions such as sodium and potassium ions are detrimental to the device performance because they induce mobile ionic charges [18]. These ions have a high diffusivity in an oxide film, which deteriorates the reliability of the device. Therefore, the deposition of the capping/barrier layers for copper interconnection using alkali-metal-free precursors is of primary importance.

This work reports on the electrodeposition of CoWP films as a capping/barrier layer for copper interconnection using alkali-metal-free precursors. The characteristics of the film properties such as the thickness, composition, and microstructure of the CoWP films have been investigated by varying the electrolyte concentration.

EXPERIMENTAL

Cobalt sulfate ($CoSO_4$), ammonium tungstate ($(NH_4)_2WO_4$), and ammonium hypophosphite ($(NH_4)H_2PO_2$) were used as the sources of cobalt, tungsten, and phosphorous, respectively. The concentrations of the cobalt, tungsten, and phosphorous precursors were varied from 0.01 to 0.09, 0.001 to 0.009, and 0.01 to 0.05 M, respectively. Ammonium citrate was used as a complexing agent to prevent spontaneous metal reduction and precipitation in the electrolyte. Citrate was chosen because it is non-toxic and has brightening, leveling, and buffering actions [19]. In all cases, the concentration of ammonium citrate was fixed at 0.2 M throughout the study. The electrolytes were obtained by dissolving the above chemicals in deionized water. The electrolytes were deaerated with nitrogen gas prior to electrodeposition of the CoWP films.

Electrodeposition was carried out using a standard three-electrode cell. A platinum-coated titanium mesh (2.5 cm^2 in size) and a saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Copper was deposited as the substrate onto a silicon wafer by PVD (physical vapor deposition). Prior to the copper deposition, a thin titanium film (~20 nm) was coated on the silicon wafer to improve the adhesion of copper to silicon. The substrate was cut into a 1×3 cm^2 rectangle and lacquered to expose 1 cm^2 for electrodeposition of the CoWP films. Before deposition, nitrogen gas was blown over the substrate to clean it. Deposition

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was carried out at a constant potential of −1.1 V versus Ag/AgCl from a stagnant electrolyte at room temperature (23±2 °C) for 5 mins. After deposition, the samples were washed with a water jet and dried with flowing nitrogen gas.

The electrochemical measurements were obtained using a computer-controlled potentiostat (VSP-Princeton Applied Research). The film thickness was measured with a surface profiler (Ambios Technology, XP-1). The composition of the films was analyzed by energy dispersive X-ray (EDX). Microstructural analysis of the films was done by using a high power X-ray diffractometer (D/max-2500 V/PC, Rigaku). The surface morphology was examined with scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Fig. 1 shows the effect of the cobalt ion concentration on the current density and film thickness. The current density monotonically increased with the cobalt ion concentration. This led to an increase in the film thickness with the cobalt ion concentration.

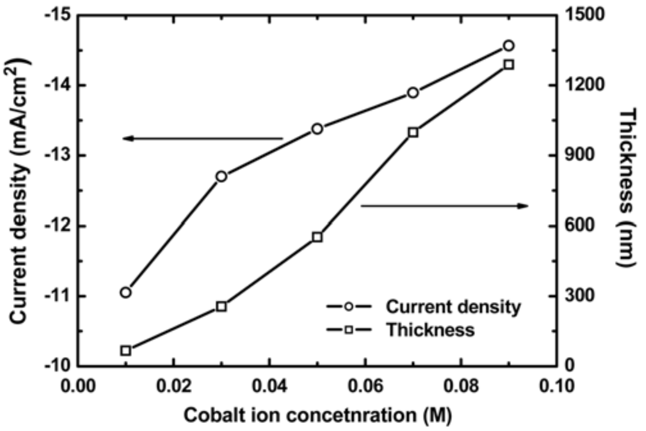


Fig. 1. Current density and film thickness as a function of cobalt ion concentration. The concentrations of tungsten and hypophosphite ions were 0.009 and 0.05 M, respectively.

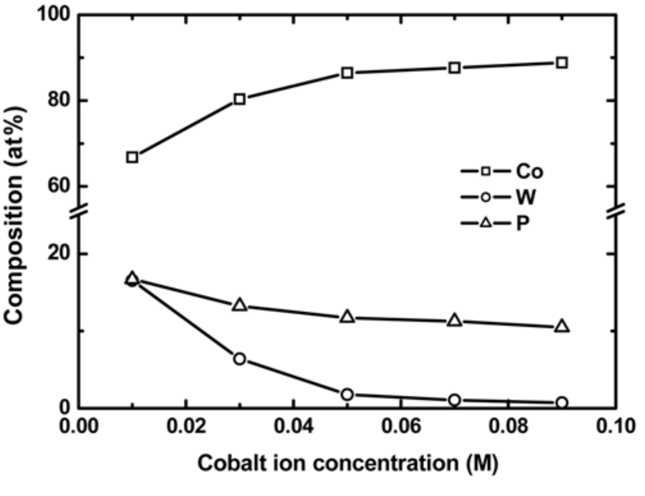


Fig. 2. Changes in the composition of CoWP films as a function of cobalt ion concentration. The concentrations of tungsten and hypophosphite ions were 0.009 and 0.05 M, respectively.

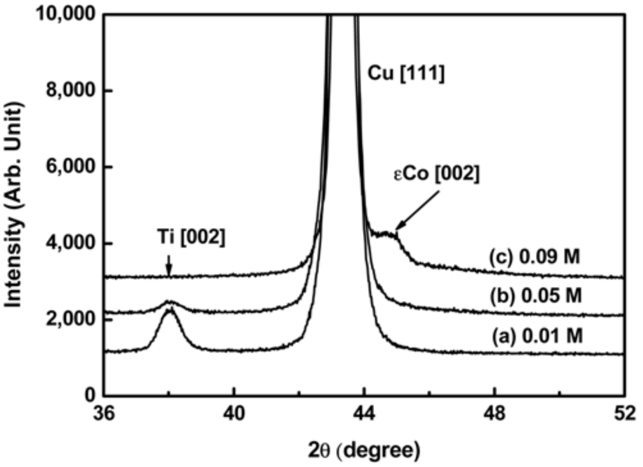


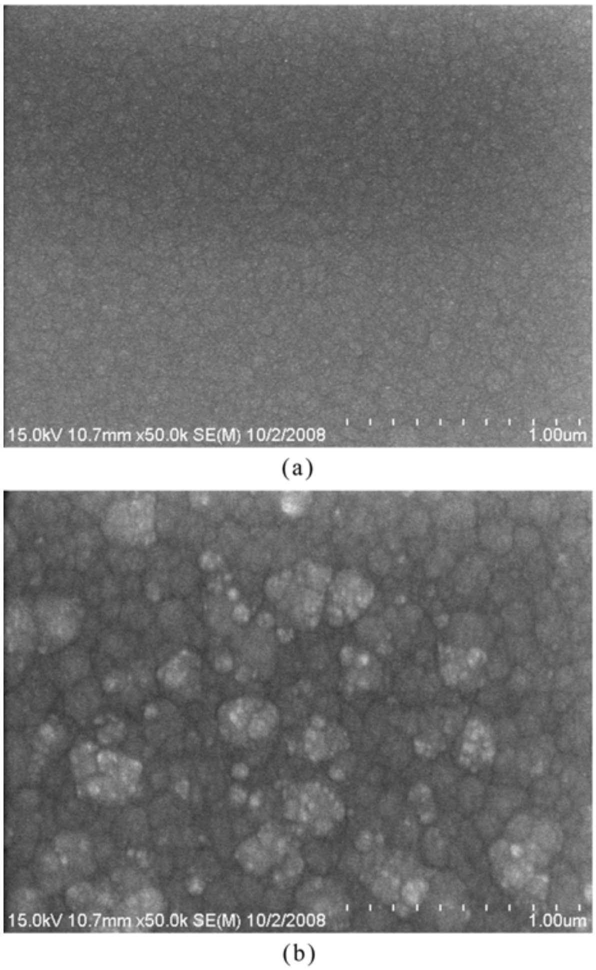
Fig. 3. XRD patterns of the CoWP films electrodeposited from the electrolyte having cobalt ion concentration of (a) 0.01, (b) 0.05, and (c) 0.09 M. The concentrations of tungsten and hypophosphite ions were 0.009 and 0.05 M, respectively.

The composition of CoWP films was greatly changed as the cobalt ion concentration varied in Fig. 2. The cobalt content increased from 67 to 89 at% when its concentration in the electrolyte was changed from 0.01 to 0.09 M. While the cobalt content in the CoWP films increased with the cobalt ion concentration, the tungsten and phosphorous contents decreased from 16 to 0.7 and 17 to 10 at%, respectively. These results suggest that the CoWP film largely consists of cobalt at high cobalt concentrations.

Fig. 3 shows X-ray diffraction patterns of the CoWP films electrodeposited from electrolytes with various cobalt ion concentrations. The strong peaks at $2\theta=43.5^{\circ}$ corresponded to copper (used as a substrate) with a preferred orientation of [111], whereas the peaks at $2\theta=38.4^{\circ}$ were related to titanium (used as an adhesion layer). These titanium peaks became weaker as the cobalt ion concentration increased because the thickness of the CoWP film increased while the thickness of titanium remained constant. The CoWP films obtained from the electrolytes containing cobalt ion concentration of 0.01 and 0.05 M did not show any cobalt-related peaks, implying that these films were amorphous. For amorphous structures, high phosphorous and tungsten content was present in these films. Other studies on electrolessly deposited CoWP films showed that the films had amorphous structures when the phosphorous content was higher than 11 at% and the tungsten content was kept below 5 at% [19,20].

The CoWP films having higher cobalt content and lower phosphorous and tungsten contents had crystallites as shown in Fig. 3(c). The XRD spectrum of the CoWP film electrodeposited from the electrolyte with higher cobalt ion concentrations showed a peak at 2θ around 44.5 due to hexagonal cobalt (εCo) with a preferred orientation of [002].

The microstructural changes in the CoWP films with respect to the cobalt ion concentration can also be examined by analyzing the surface morphology of the films. Fig. 4 shows the SEM images of the CoWP films obtained from electrolytes having cobalt ion concentrations of 0.01 and 0.09 M. The electrolyte with the lower cobalt ion concentration produced an amorphous CoWP film having



(a)

(b)

Fig. 4. SEM images of the CoWP films electrodeposited from the electrolyte having cobalt ion concentration of (a) 0.01 and (b) 0.09 M. The concentrations of tungsten and hypophosphite ions were 0.009 and 0.05 M, respectively.

a smooth surface with no crystallites (Fig. 4(a)). On the other hand, the high cobalt ion concentration produced a crystalline CoWP film having spherical crystallites (Fig. 4(b)) whose size was in the range of 80~150 nm.

Figs. 5 and 6 show the changes in the current density and film thickness as functions of tungstate and hypophosphite ion concentrations, respectively. Both the current density and film thickness increased with the tungstate and hypophosphite ion concentrations. It is known that tungsten and phosphorous are unable to be electrodeposited individually from aqueous electrolyte, but they are codeposited from aqueous electrolyte containing iron-group metals, which is referred to as "induced codeposition" [21]. Therefore, an increase in the film thickness with tungstate and hypophosphite ion concentrations suggests that the rate of induced codeposition of a CoWP film is enhanced by increasing the tungstate and/or hypophosphite ion concentrations under the conditions employed in this study.

Compositional changes in the CoWP film with tungstate and hypophosphite ion concentrations are given in Figs. 7 and 8, respectively. It is seen from Fig. 7 that the tungsten content in the CoWP film increased from 1.2 to 8.6 at% as the tungstate ion concentra-

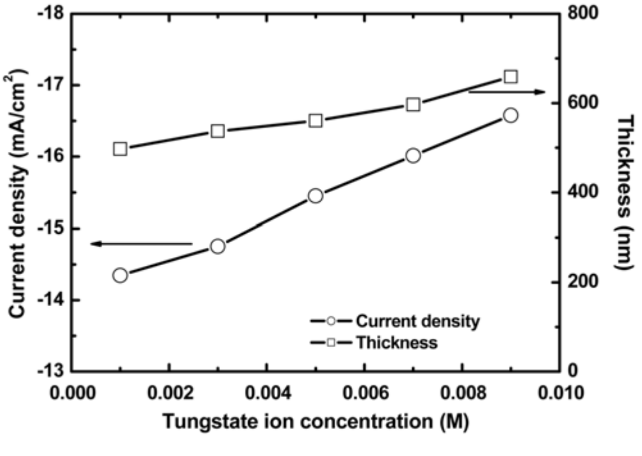


Fig. 5. Current density and film thickness as a function of tungstate ion concentration. The concentrations of cobalt and hypophosphite ions were 0.05 M.

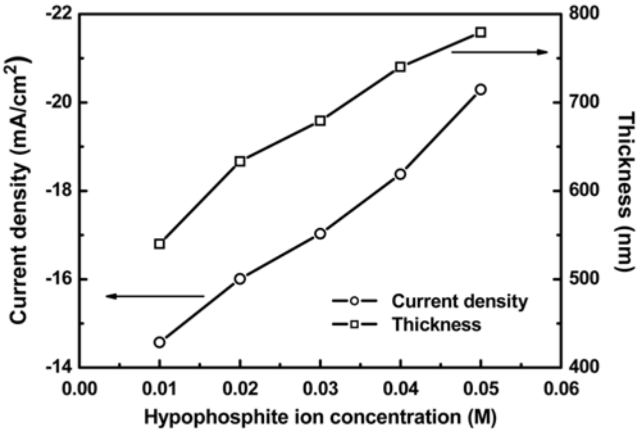


Fig. 6. Current density and film thickness as a function of hypophosphite ion concentration. The concentrations of cobalt and tungstate ions were 0.05 and 0.009 M, respectively.

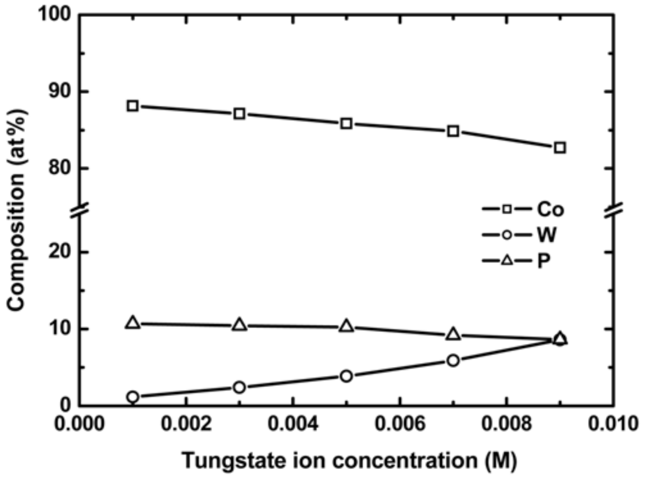


Fig. 7. Changes in the composition of CoWP films as a function of tungstate ion concentration. The concentrations of cobalt and hypophosphite ions were 0.05 M.

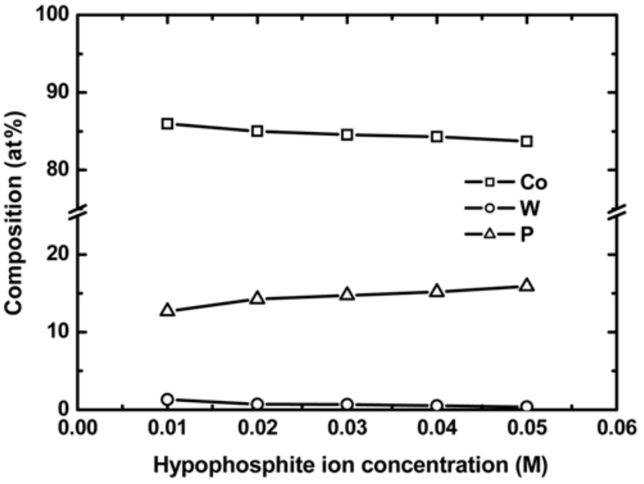


Fig. 8. Changes in the composition of CoWP films as a function of hypophosphite ion concentration. The concentrations of cobalt and tungstate ions were 0.05 and 0.009 M, respectively.

tion was raised from 0.001 to 0.009 M. While the tungsten content in the film increased more than seven times of its original value, the extent of variation for the cobalt and phosphorous contents was much less. The phosphorous content in the film increased from 13 to 16 at% when its concentration in the electrolyte increased from 0.01 to 0.05 M as seen in Fig. 8. Under these conditions, the cobalt and tungsten contents decreased from 86 to 84 and 1.3 to 0.4 at%, respectively. Therefore, it can be said that the cobalt content in the CoWP film has very little sensitivity to variations in the tungstate and hypophosphite ion concentrations.

The XRD spectra of the CoWP films electrodeposited with varying tungstate and hypophosphite ion concentrations showed only copper peaks and no cobalt-related peaks (not shown here), implying that amorphous CoWP films were obtained under these conditions. As mentioned earlier, the grain boundaries in the capping/barrier layers provide diffusion pathways to copper, which deteriorates the device performance. To stuff the grain boundaries of the CoWP films, tungsten and phosphorous were added during the electrodeposition of the CoWP films in this study. Therefore, sufficient tungsten and phosphorous content was necessary in the film in order to make amorphous film structures. When either the tungstate or hypophosphite ion concentration was varied, the cobalt ion concentration was fixed to 0.05 M. Under these conditions, the tungsten and hypophosphite contents were high enough to fill the grain boundaries of the CoWP films. When the tungsten and phosphorous content was relatively low in the film ($Co_{88.8}W_{0.7}P_{10.5}$) at a high cobalt ion concentration of 0.09 M, the CoWP film was crystalline (see Fig. 3(c)).

CONCLUSIONS

The electrodeposition of CoWP films using alkali-metal-free precursors was demonstrated, and the effects of electrolyte concentration on the thickness, composition, and microstructure of the CoWP films were investigated.

The current density and the film thickness increased with increasing cobalt ion concentration. Increasing the tungstate and hypophosphite ion concentrations also increased the current density and the film thickness, implying that the addition of tungstate and/or hypophosphite ions would enhance the electrodeposition rate of the CoWP film.

As the cobalt ion concentration increased, the cobalt content in the film increased but the tungsten and phosphorous contents greatly decreased. The tungsten and phosphorous content also increased with increasing tungstate and hypophosphite ion concentrations, respectively.

The microstructures of the CoWP films electrodeposited using alkali-metal-free precursors depended strongly on the tungsten and phosphorous content in the film. The CoWP film had a crystalline structure when the tungsten and phosphorous content was relatively low, for example $Co_{88.8}W_{0.7}P_{10.5}$. Other than this condition, all of the other CoWP films were amorphous.

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