ORIGINAL PAPER

Electrodeposition of CoWP film II. Effect of electrolyte concentration

**S. M. S. I. Dulal · Chee Burm Shin ·
Joon Yong Sung · Chang-Koo Kim**

Abstract CoWP films were electrodeposited on copper-coated silicon wafers from citrate electrolyte containing cobalt sulphate, sodium tungstate and sodium hypophosphite at room temperature potentiostatically. The effects of electrolyte concentration on thickness, composition and microstructure of the films were studied. It was observed that the deposition current density and thickness increased with increasing cobalt and hypophosphite ion concentrations, whereas an increase in tungstate ion concentration resulted in a decrease in current density and thickness. Films with larger variations of cobalt (from 64 to 83 at.%), tungsten (from 0.5 to 24 at.%) and phosphorus (from 6 to 21 at.%) were electrodeposited by controlling the concentrations of the electrolytes. X-ray diffraction studies suggested that films containing ~ 20 at.% phosphorus were amorphous while films with lower phosphorus content were crystalline. SEM and AFM examinations showed that the size of crystallites and surface roughness were mainly dependent on the amount of phosphorus present in the films.

S. M. S. I. Dulal · C. B. Shin · C.-K. Kim (✉)
Department of Chemical Engineering and Division of Energy Systems Research, Ajou University, Suwon 443-749, Korea
e-mail: changkoo@ajou.ac.kr

Present Address:
S. M. S. I. Dulal (✉)
Department of Materials Science and Technology, University of Rajshahi, Rajshahi 6205, Bangladesh
e-mail: dulal_smsi@yahoo.com

J. Y. Sung
Center for Clean Technology, Yonsei University, Seoul 120-749, Korea

1 Introduction

CoWP films have promising applications as a barrier/capping layer of copper interconnections in microelectronic devices and microelectromechanical systems (MEMS) to prevent copper from oxidation and diffusion [1–9]. CoWP films can also be useful for other applications. CoP is known to have good magnetic properties and has recently been used in integrated sensors and inductors [10, 11]. CoW films show some promising physical and mechanical properties such as exceptional hardness, wear and corrosion resistances [12, 13]. Therefore, it is envisaged that, with appropriate composition CoWP films may exhibit superior and unique properties and can be utilized as coatings in sophisticated electronic and automobile industries, rocketry and space technology.

There are some reports in the literature on the fabrication of CoWP films on a copper substrate by electroless deposition from aqueous solution [1–9]. However, electroless deposition is very selective and requires higher processing temperature. Sometimes, the copper substrate needs to be activated by a catalyst to initiate the deposition process. It has been found that phosphorus in the CoWP layers plays a very important role against the diffusion of copper by 'stuffing' the grain boundaries of the barrier/capping layers, but layers containing more than 12 at.% phosphorus cannot be plated by electroless deposition [2]. On the other hand, electrodeposition offers lower processing temperature, better control over the deposition technique and thus a wide range of compositions.

It has been claimed that tungsten and phosphorus cannot be electrodeposited individually from aqueous electrolyte [12]. However, tungsten and phosphorus can be co-deposited from aqueous electrolyte containing iron group metals (Fe, Co, Ni), which is termed 'induced co-deposition' [12]. There are also some reports in the literature on the electrodeposition of CoP [14–19], NiCoP [14, 20] and CoW [21, 22] films.

The present study aims at the electrodeposition of CoWP thin films on copper from aqueous solution at room temperature. Electrochemical aspects of the deposition of this film have recently been reported [23]. The properties of ternary films like CoWP are crucially dependent on the relative amount of the constituent components. For an effective barrier layer for copper interconnection CoWP film should contain a small amount of tungsten (<5 at.%) and a reasonably high amount of phosphorus. On the other hand, the tungsten content in the film should be as high as ~50 at.% if it is intended for use as a hard coating. Therefore, it is important to control and modulate the composition of CoWP films for particular uses. One way to do this is to control the concentration of the electrolyte. This paper reports the effect of bath concentration on the composition and microstructure of CoWP films electroplated from a citrate electrolyte by a potentiostatic method.

2 Experimental

Polarisation behaviour of induced codeposition of cobalt, tungsten and phosphorus at a copper disc electrode of geometrical area of 0.95 cm^2 and of 99.9999% purity was studied by cyclic voltammetry and CoWP films were electrodeposited on copper-coated silicon wafers by a potentiostatic method. A potentiostatic technique was preferred because it was found previously that the surface quality of the deposit plated by this method was better than that of a surface plated under galvanostatic conditions [23]. CoSO$_4$·7H$_2$O, Na$_2$WO$_4$·2H$_2$O and NaH$_2$PO$_2$·H$_2$O were used as the sources of cobalt, tungsten and phosphorus, respectively. Tri-sodium citrate (TSC) was used as a complexing agent and its concentration was 0.3 M in all electrolytes. Tri-sodium citrate was chosen because it was non-toxic and had brightening, levelling and buffering actions [24–27]. Moreover, citrate electrolyte has recently been used for precision electrodeposition [27, 28]. The electrolytes were prepared by dissolving appropriate amounts of the chemicals in de-ionised water. The pH of the electrolyte was 6.9, although it varied slightly (±0.1) depending on the concentration of the solution. Approximately 200 ml solution was taken in a 250 ml vial. Prior to cyclic voltammetry experiments and electrodeposition of CoWP films, the electrolytes were de-aerated by nitrogen

gas for 5 min. The chemicals were of the highest purity supplied by Sigma-Aldrich and were used as received.

Electrodeposition was performed using a standard three-electrode cell where a platinum coated titanium mesh of 2.5 cm^2 was used as a counter electrode. The substrate was copper, deposited by sputtering on a silicon wafer. The wafer was cut into 1 cm × 3 cm sized pieces with a diamond saw and lacquered to expose 1 cm^2 for plating CoWP films. The substrate was cleaned by blowing with nitrogen gas before deposition. A saturated Ag/AgCl electrode was used as a reference electrode. The deposition was carried out at a constant potential of –1 V versus Ag/AgCl from stagnant solution at room temperature (23 ± 3 °C) for 5 min. After deposition, the samples were washed with a water jet and dried by blowing with nitrogen gas. The surface of the plated films appeared flat and bright.

The electrochemical measurements were conducted using a computer-controlled potentiostat (VSP-Princeton Applied Research). The thickness of the films was measured by a surface profiler (Alpha Step). The compositional analysis was carried out using energy dispersive X-ray diffraction (EDX). Structural and morphological studies were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3 Results and discussion

3.1 Cyclic voltammetry

Figure 1 shows cyclic voltammograms of aqueous electrolytes containing (i) 0.07 M CoSO$_4$ and 0.3 M TSC (ii) 0.07 M CoSO$_4$, 0.01 M Na$_2$WO$_4$ and 0.3 M TSC, (iii) 0.07 M CoSO$_4$, 0.04 M NaH$_2$PO$_2$ and 0.3 M TSC and (iv) 0.07 M CoSO$_4$, 0.01 M Na$_2$WO$_4$, 0.04 M NaH$_2$PO$_2$ and 0.3 M TSC on a copper disc electrode at room temperature. In this case, the potential was scanned negatively from –0.1 V to –1.5 V at 30 mV s^{-1} and ended at –0.1 V. The potential was not swept more positive than –0.1 V because copper is known to dissolve beyond this potential [28].
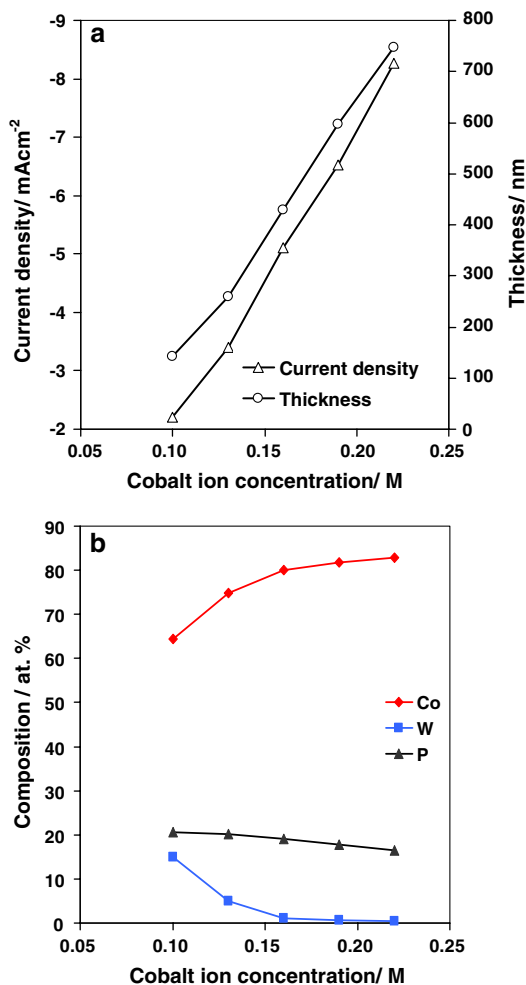
On the forward scan the voltammograms show a sudden increase in current at a potential of approximately –0.95 V versus the Ag/AgCl reference electrode which is the starting point of the reduction of the electroactive species. Peaks develop at a potential of –1.14 V in the case of hypophosphite containing electrolytes and the evolution of hydrogen occurs at –1.17 V. Therefore, it can be expected that there will be little or no hydrogen evolution if CoWP films are deposited at a potential more positive than –1.17 V. The polarisation curves of the cobalt, and the cobalt and tungstate containing electrolytes do not show a
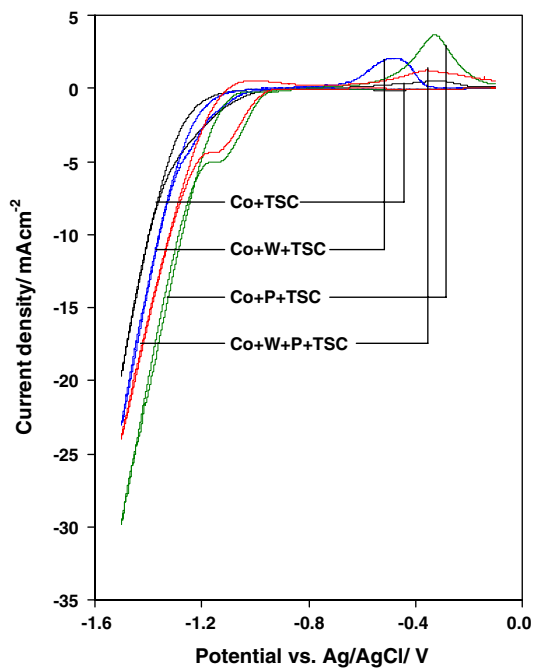
Fig. 1 Cyclic voltammograms of aqueous electrolytes containing (i) 0.07 M $CoSO_4$ and 0.3 M TSC (ii) 0.07 M $CoSO_4$, 0.01 M Na_2WO_4 and 0.3 M TSC, (iii) 0.07 M $CoSO_4$, 0.04 M NaH_2PO_2 and 0.3 M TSC and (iv) 0.07 M $CoSO_4$, 0.01 M Na_2WO_4, 0.04 M NaH_2PO_2 and 0.3 M TSC on a copper disc electrode. The scan rate was 30 mV s^{-1}

Fig. 2 Effect of cobalt ion concentration on (**a**) deposition current density and film thickness and (**b**) composition of CoWP films electrodeposited by applying a constant potential of –1 V at room temperature. The concentrations of tungstate and hypophosphite ions were 0.001 and 0.03 M, respectively. Deposition time was 5 min
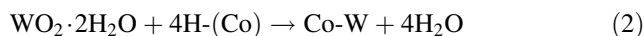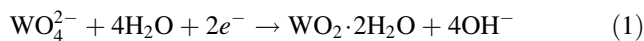
peak or plateau to indicate a limiting current. It has recently been reported that linear sweep voltammetry at various scan rates suggests that the induced codeposition of cobalt, tungsten and phosphorus from an electrolyte containing cobalt sulphate, sodium tungstate, sodium hypophosphite and tri-sodium citrate occurs via a nucleation process under mass transfer control [23]. Figure 1 also shows that dissolution of the deposits starts at around –0.8 V on the reverse scan when the electrolytes contain cobalt, and cobalt and hypophosphite ions. On the other hand, the stripping potential shifts cathodically (at around –1.0 V) in the cases of tungstate containing electrolytes.

The polarisation curves in the cathodic region show that at a given over-potential the highest current is found when the electrolyte contains cobalt and hypophosphite ions. The addition of tungstate ions results in a reduction in cathodic current. This suggests that tungstate ions have an inhibitive action on the reduction of the species, which might be due to the fact that the induced co-deposition of tungsten occurs through both electrochemical and chemical reactions. Initially an oxide of tungsten is deposited on the substrate, which is catalyzed by iron group metals (in this case cobalt) for subsequent reduction to tungsten. Ibrahim et al. [22] proposed that CoW alloy formation takes place through electrochemical reduction of tungstate ion to tungstate oxide and then chemical reduction of tungstate

oxide to metallic tungsten according to the following equations,

$$WO_4^{2-} + 4H_2O + 2e^- \rightarrow WO_2 \cdot 2H_2O + 4OH^- \tag{1}$$

$$WO_2 \cdot 2H_2O + 4H\text{-}(Co) \rightarrow Co\text{-}W + 4H_2O \tag{2}$$

where H-(Co) indicates a hydrogen atom bonded to the d-band vacancy of cobalt.

The deposition of CoWP occurs along with hydrogen evolution at potentials more negative than –1.17 V in all cases (Fig. 1). Therefore, from the polarisation curves in the cathodic region it cannot be concluded definitely in which case the highest amount of deposition occurs. Therefore, the stripping charges from the polarisation curves in the anodic region have been calculated and it has been found that the stripping charges for the cobalt, cobalt
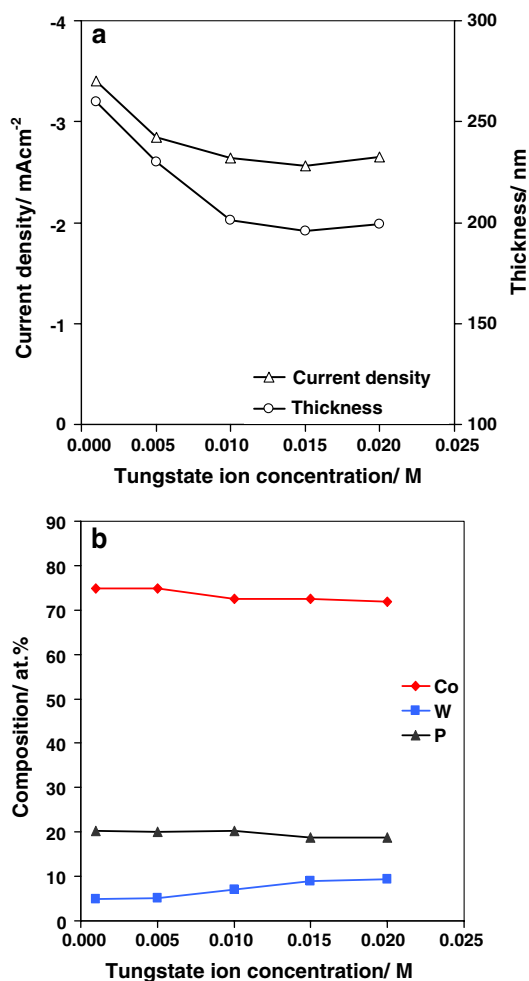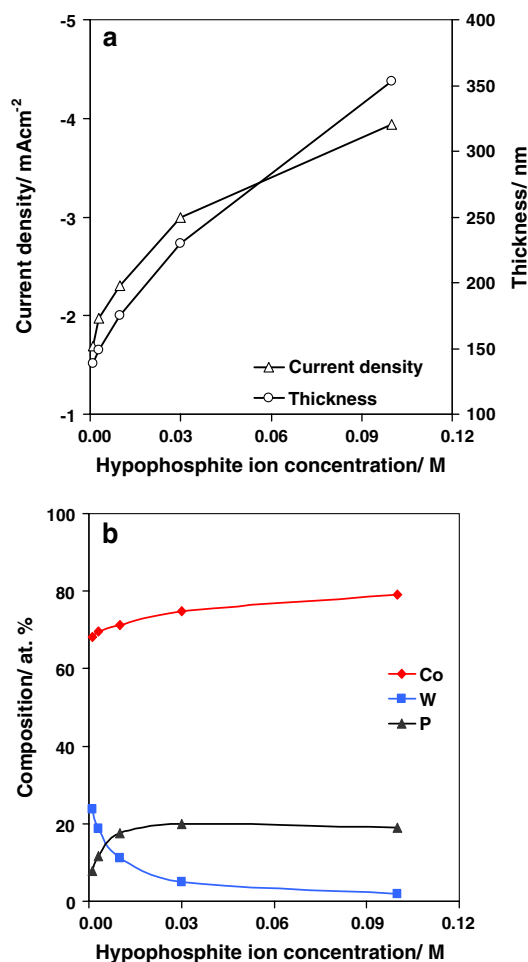
Fig. 3 Effect of tungstate ion concentration on (**a**) deposition current density and film thickness and (**b**) composition of CoWP films electrodeposited by applying a constant potential of –1 V at room temperature. The concentrations of cobalt and hypophosphite ions were 0.13 and 0.03 M, respectively. Deposition time was 5 min

Fig. 4 Effect of hypophosphite ion concentration on (**a**) deposition current density and film thickness and (**b**) composition of CoWP films electrodeposited by applying a constant potential of –1 V at room temperature. The concentrations of cobalt and tungstate ions were 0.13 and 0.005 M, respectively. Deposition time was 5 min

and tungstate, cobalt and hypophosphite, and cobalt, tungstate and hypophosphite ions containing electrolytes are 4.66, 13.74, 24.59 and 17.54 mC, respectively. These results confirm that the highest amount of deposition occurs when the electrolyte contains cobalt and hypophosphite ions.

3.2 Effect of cobalt ion concentration on thickness and composition

Figure 2 shows the effect of cobalt ion concentration on current density, deposit thickness and film composition. The current was recorded at the 1st, 3rd and 5th minute and the average of these data is presented in the figure. It was observed that the current density fluctuated about ±0.05 mA cm^{-2}. Figure 2a shows that the current density increases linearly with cobalt ion concentration which

suggests that the thickness of the deposit increases proportionally. Figure 2a also shows that the thickness increases almost linearly with increasing cobalt ion concentration in the electrolyte.

The composition of the plated CoWP films at various cobalt ion concentrations is presented in Fig. 2b. The cobalt content increases from 64 to 83 at.% when its concentration in the electrolyte is varied from 0.10 to 0.22 M. The increase in the relative amount of cobalt in the deposit is rather steep when the concentration of cobalt ion is increased from 0.10 M to 0.16 M. A further increase in cobalt ion concentration from 0.16 to 0.22 M in the electrolyte results in a slow increase of its content in the deposit. The effect of cobalt ion concentration on tungsten content is opposite. Tungsten content decreases from 15 to 0.50 at.% with increasing cobalt ion concentration. The relative amount of phosphorus in the film also decreases from 21 to 16 at.%.
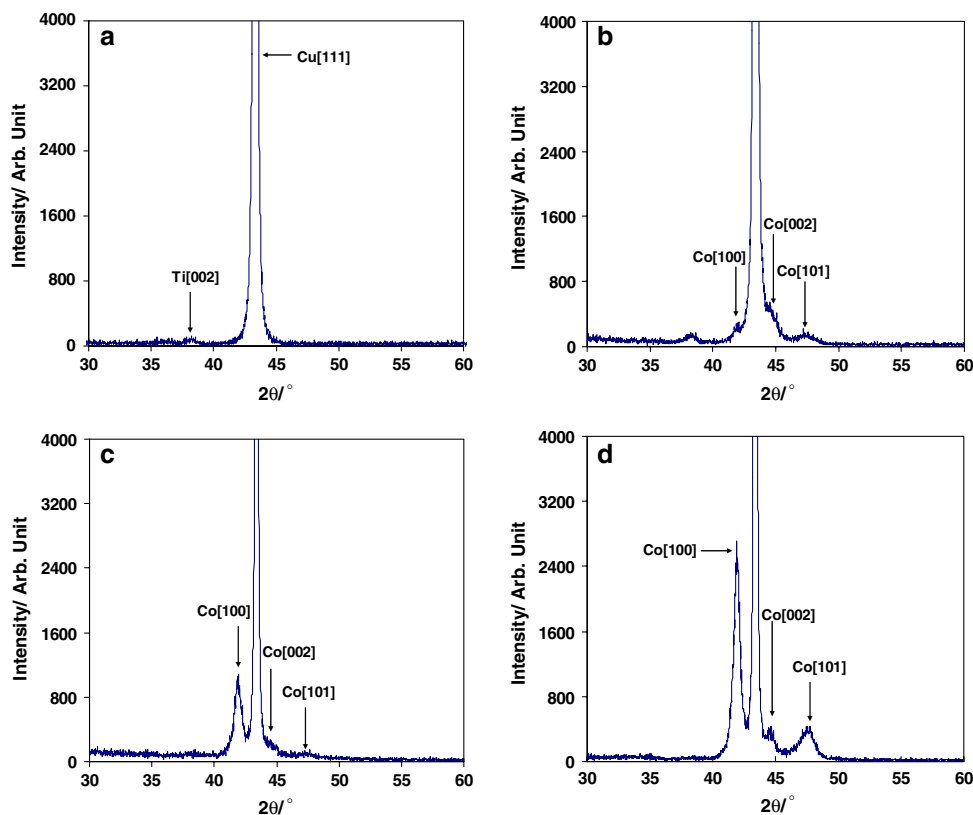
3.3 Effect of tungstate ion concentration on thickness and composition

The effect of tungstate ion concentration on deposition current density, thickness and composition of CoWP thin films is shown in Fig. 3. Unlike for the cobalt ion, the current density decreases with increase in tungstate ion concentration. Figure 3a also shows that the deposit thickness decreases almost proportionally with decreasing current density (with increasing tungstate ion concentration) which is expected, because with decreasing current density the deposition rate also decreases. As observed in the cyclic voltammograms (Fig. 1), the addition of tungstate ions to the cobalt and hypophosphite containing solution reduces the cathodic current due to some inhibitive action of this species on the electrodeposition of CoWP, it is expected that the current density and thickness would decrease with increase in tungstate ion concentration. This may be due to the two-step reduction of tungstate ions to elemental tungsten as explained in Sect. 3.1.

Figure 3b shows the dependence of CoWP film composition on tungstate ion concentration in the bath. Tungsten content in the film increases from approximately 5 to 10 at.% when its concentration in the electrolyte is varied from 0.001 to 0.02 M. On the other hand, the amounts of both cobalt and phosphorus decrease slightly.

3.4 Effect of hypophosphite ion concentration on thickness and composition

The dependences of deposition current density, deposit thickness and composition of CoWP thin films on hypophosphite ion concentration in the solution are depicted in Fig. 4. This shows a steep increase in current density and deposit thickness with increase in hypophosphite ion concentration. In this case, the thickness curve is less steep when the hypophosphite ion concentration exceeds 0.03 M.

Figure 4b shows the effect of hypophosphite ion concentration on the composition of CoWP films. Phosphorus content in the layer increases sharply when the hypophosphite ion concentration is increased from 0.001 to 0.01 M. Further increase in hypophosphite ion concentration does not increase the phosphorus content in the layer. This means that there is a saturated situation beyond which further increase in phosphorus in the film is not possible under the deposition conditions used.

Figure 4b also shows that tungsten content in the deposit decreases with hypophosphite ion concentration in the electrolyte but the relative amount of cobalt in the film increases. This suggests that hypophosphite in the electrolyte facilitates induced co-deposition, which is in good agreement with the results of cyclic voltammetry experiments (Fig. 1). Detailed electrochemical studies also show
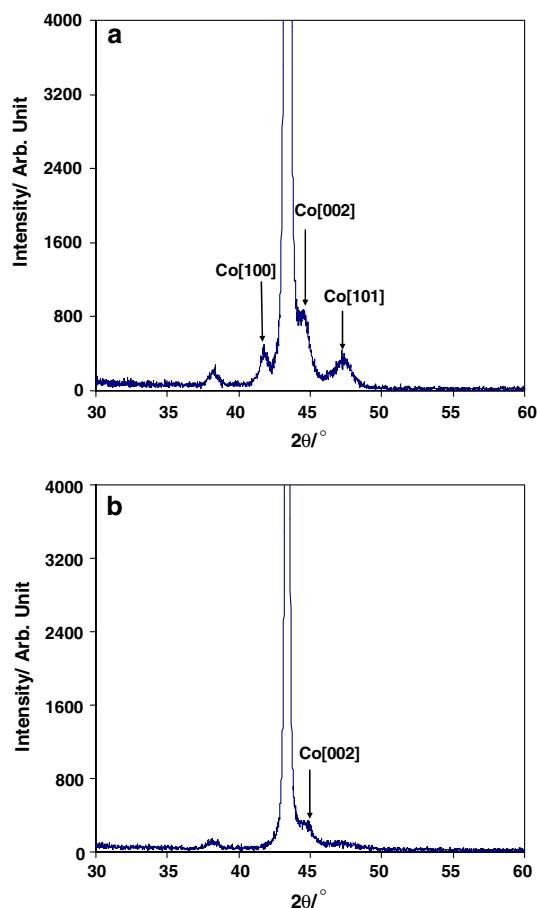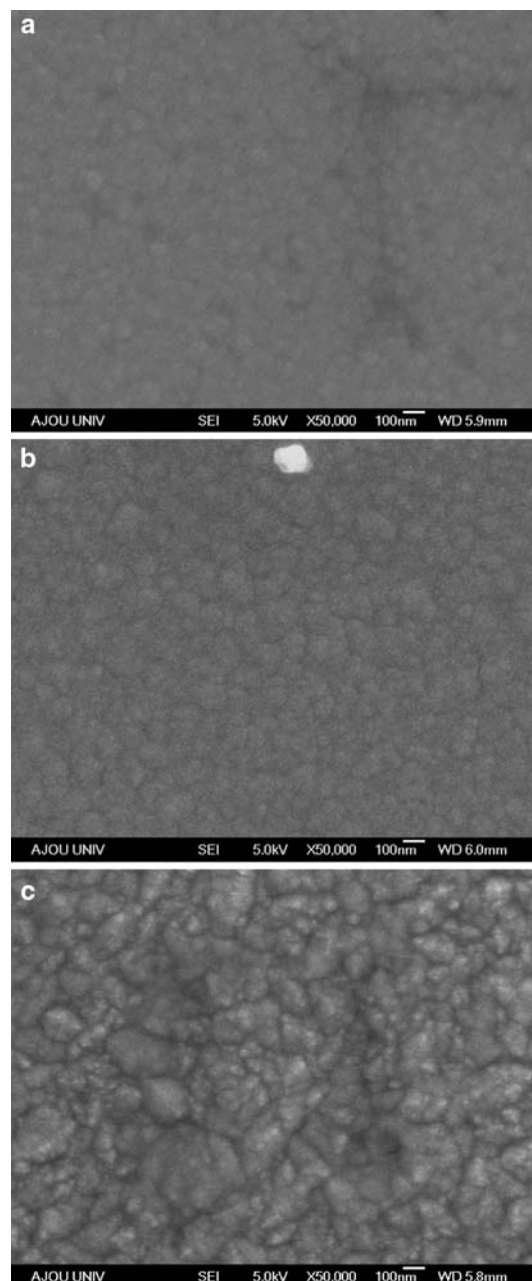
Fig. 6 XRD spectra of CoWP films containing various amounts of constituent elements: (**a**) $Co_{0.69}W_{0.19}P_{0.12}$ and (**b**) $Co_{0.79}W_{0.02}P_{0.19}$. The films were prepared by varying the concentration of hypophosphite ions in the solution (the deposition conditions have been given in the caption of Fig. 4)

that it takes less energy to initiate electrocrystallisation of cobalt (and cobalt–tungsten) from a citrate electrolyte when hypophosphite ions are present in the solution [23].

3.5 Dependence of microstructures on composition

XRD spectra of the substrate and CoWP films with varied amount of the constituent elements are shown in Fig. 5. In this case, the composition of the film was controlled by varying the cobalt ion concentration in the electrolyte. The substrate copper has a strong crystallographic orientation of [111]. There is also a small peak at $2\theta = 38.4°$ on the XRD spectrum of the substrate (Fig. 5a), which is related to Ti[002] of the seed layer.

XRD spectra of $Co_{0.64}W_{0.15}P_{0.21}$ (Film I), $Co_{0.80}W_{0.01}P_{0.19}$ (Film II) and $Co_{0.825}W_{0.005}P_{0.17}$ (Film III) samples (Fig. 5b, c and d, respectively) suggest the presence of hcp cobalt in the deposit. Three small peaks of hcp cobalt with no strong preferred orientation suggest an

Fig. 7 SEM images of CoWP films containing various amounts of constituent elements, (**a**) $Co_{0.64}W_{0.15}P_{0.21}$, (**b**) $Co_{0.80}W_{0.01}P_{0.19}$ and (**c**) $Co_{0.825}W_{0.005}P_{0.17}$. The thicknesses of these films are 143, 430 and 747 nm, respectively

amorphous structure of Film I. The films, however, become crystalline with strong preferred orientation of εCo [100] with increasing cobalt and decreasing tungsten and phosphorus contents in them (Fig. 5c and d). An amorphous structure of electrolessly deposited CoWP films was obtained when the phosphorus content in the film exceeded 11 at.%, keeping the tungsten content less than 5 at.% [6, 29]. However, the present study suggests that the electrochemically deposited films are crystalline in nature even if
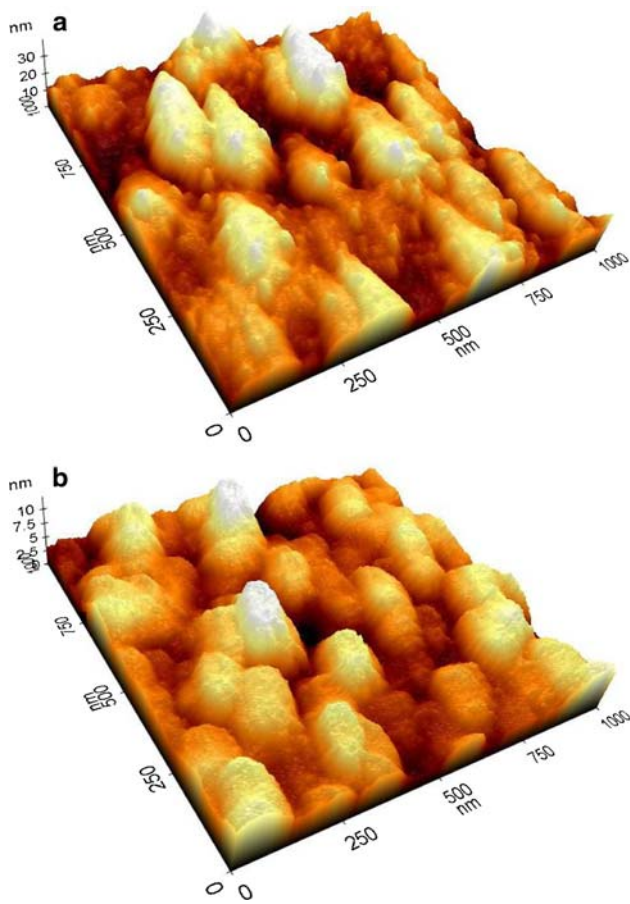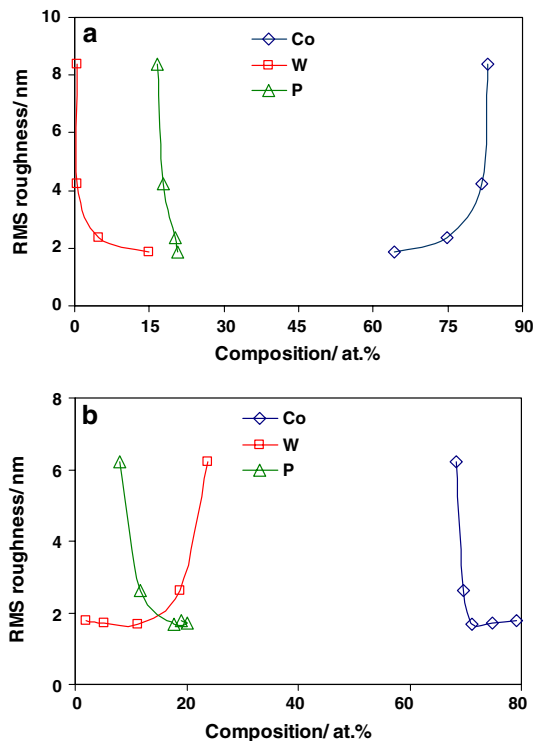
Fig. 8 Typical 3D AFM images of CoWP films with phosphorus contents of (**a**) 8 at.% and (**b**) 19 at.%

Fig. 9 Dependence of roughness on the compositions of CoWP films when (**a**) the films were prepared by varying the concentration of cobalt ions in the solution (the deposition conditions have been given in the caption of Fig. 2) and (**b**) the films were prepared by varying the concentration of hypophosphite ions in the solution (the deposition conditions have been given in the caption of Fig. 4)

Fig. 10 Surface roughness as a function of thickness of CoWP films produced by varying the concentrations of cobalt (solid line) and hypophosphite (dashed line) ions

they contain a reasonably high amount of phosphorus with a tungsten content around 1 at.% (Films II and III).
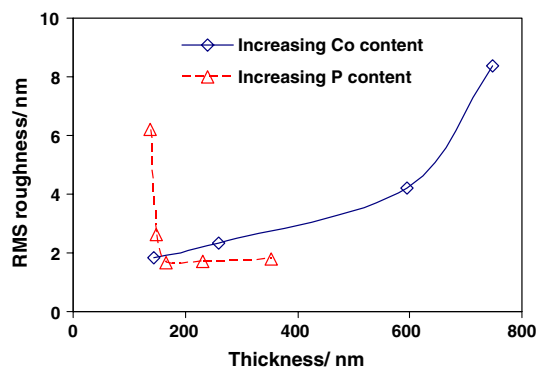
Although phosphorus and tungsten have a synergistic effect on the crystallinity of CoWP films, this mainly depends on the amount of phosphorus present in the deposit. XRD spectra of the other two samples which were deposited by varying the concentration of hypophosphite ion in the electrolyte (Fig. 6), suggest that $Co_{0.69}W_{0.19}P_{0.12}$ (Film IV) film is polycrystalline even though it contains higher amounts of tungsten and phosphorus, but $Co_{0.79}W_{0.02}P_{0.19}$ (Film V) is amorphous although it contains more cobalt than the former one. It is noticeable that the phosphorus content in Films II and V is the same, but the tungsten content is just 1 at.% more in Film V, which makes it amorphous.

3.6 Surface morphology and roughness

The SEM images of the surfaces of Films I, II and III are shown in Fig. 7. These films were deposited from electrolytes of various cobalt ion concentrations. The images

suggest that the films have typical spherical nodular structure with dense coverage. However, the crystallites get larger with the increase in cobalt content in the solutions as well as in the films, which is due to faster growth under the potentiostatic conditions employed. However, there may also be some effect of thickness as with increasing cobalt ion concentration in the electrolyte the thicknesses of the films also increase. SEM images of the films deposited by varying tungstate and hypophosphite ion concentrations

also have typical spherical nodular structures which look similar to that shown in Fig. 7b.

The roughnesses of these surfaces were measured using AFM. Figure 8 shows typical 3D AFM images of two samples with low (8 at.%) (Fig. 8a) and high (19 at.%) (Fig. 8b) phosphorus contents and Fig. 9 shows the dependence of roughness on the composition of CoWP films. Figure 9a shows the roughness of CoWP samples prepared by varying the concentration of cobalt ions. It suggests that the roughness increases with increasing cobalt and decreasing tungsten and phosphorus contents in the films as well as increasing size of the crystallites. On the other hand, Fig. 9b shows the dependence of roughness on composition when the samples were produced by varying the concentration of hypophosphite ions. It shows a decrease in roughness with increasing phosphorus and cobalt contents in the films. The apparent discrepancy of the dependency of roughness on cobalt content can be explained in that the increased phosphorus in the films make them less crystalline with smaller crystallites even though there is also an increase in cobalt content. Therefore, it can be concluded that the roughness is mainly dependent on the crystalline states of the films and decreases when the films go from crystalline to amorphous. In electrolessly deposited CoWP films, it was observed that phosphorus and tungsten mainly accumulated in the grain boundaries of hexagonal cobalt as the solubility of phosphorus and tungsten in εCo is less than 1 at.% [2, 29]. More phosphorus (and/or tungsten) in the films thus help to fill the grain boundaries and defect points which eventually decreases the roughness.

It is well-known that the roughness is also dependent on the thickness of the electrodeposited films. To see if thickness has a more prominent effect on roughness than the crystalline states, plots of thickness versus roughness are given in Fig. 10. In this figure the roughness of two sets of samples produced by varying the concentrations of cobalt (solid line) and hypophosphite (dashed line) ions, respectively, are presented. The roughness increases with thickness when the cobalt content in the film increases. The roughness, however, decreases with increase in thickness when the phosphorus content in the film increases. As discussed previously, CoWP films become amorphous with decreasing cobalt or increasing phosphorus content. Therefore, the crystalline state, rather than the thickness, has the major influence on the roughness of the electrodeposited CoWP films.

4 Conclusions

CoWP films were electrodeposited on copper-coated silicon wafers from a citrate electrolyte containing cobalt sulphate, sodium tungstate and sodium hypophosphite at room temperature. The deposition was carried out by a potentiostatic method by applying a constant potential of −1 V with respect to a Ag/AgCl reference electrode. The effects of electrolyte concentration on thickness, composition and microstructure of the films were studied. The deposition current density and thickness increased with increasing cobalt and hypophosphite ion concentrations in the electrolytes, whereas increase in tungstate ion concentration resulted in a decrease in current density and thickness. Films with larger variations of cobalt (from 64 to 83 at.%), tungsten (from 0.5 to 24 at.%) and phosphorus (from 6 to 20 at.%) were electrodeposited by controlling the concentrations of the electrolytes. X-ray diffraction studies suggested that CoWP films containing ∼20 at.% phosphorus were amorphous while films with lower phosphorus content were crystalline. The crystalline films contained hcp cobalt with strong preferred orientation of [100]. SEM images suggested that the films had a spherical nodular structure with good coverage. The crystallites became larger with the increase in cobalt content in the film. AFM examinations showed that the surface roughness was mainly dependent on the crystalline state and increased with decreasing phosphorus content in the films.

References

1. Shacham-Diamand Y, Sverdlov Y (2000) Microelectron Eng 50:525
2. Kohn A, Eizenberg M, Shacham-Diamand Y, Sverdlov Y (2001) Mater Sci Eng A 302:18
3. Petrov N, Sverdlov Y, Sacham-Diamand Y (2002) J Electrochem Soc 149:C187
4. Hu C-K, Gignac L, Rosenberg R, Liniger E, Rubino J, Sambucetti C, Stamper A, Domenicucci A, Chen X (2003) Microelectron Eng 70:406
5. Kohn A, Eizenberg M, Shacham-Diamand Y (2003) J Appl Phys 94:3015
6. Gambino J, Wynne J, Gill J, Mongeon S, Meatyard D, Lee B, Bamnolker H, Hall L, Li N, Hernandez M, Little P, Hamed M, Ivanov I, Gan CL (2006) Microelectron Eng 83:2059
7. Decorps T, Haumesser PH, Olivier S, Roule A, Joulaud M, Pollet O, Avale X, Passemard G (2006) Microelectron Eng 83:2082
8. Sverdlov Y, Bogush V, Shacham-Diamand Y (2006) Microelectron Eng 83:2243
9. Hu C-K, Canaperi D, Chen ST, Gignac LM, Kaldor S, Krishnan M, Malhotra SG, Liniger E, Lloyd JR, Rath DL, Restaino D, Rosenberg R, Rubino J, Seo S-C, Simon A, Smith S, Tseng W-T (2006) Thin Solid Films 504:274
10. Perez L, Aroca C, Sanchez P, Lopez E, Sanchez MC (2004) Sensors Actuators A 109:208

11. Ruythooren W, Beyne E, Celis J-P, Boeck J-D (2002), IEEE Trans Magn 38:3498
12. Brenner A (1963) Electrodeposition of alloys: principles and practices. Academic Press, New York
13. Donten M, Gromulski T, Stojek Z (1998) J Alloys Compd 279:272
14. Djokic SS (1999) J Electrochem Soc 146:1824
15. Jurado RM, Gonzalez JA, Riveira JM (1999) J Magn Magn Mater 196–197:246
16. Silva RCD, Santos EMD, Sartorelli ML, Sinnecker JP, Gundel A, Sommer RL, Pasa AA (2004) J Magn Magn Mater 272–276:1460
17. Silva RCD, Pasa AA, Mallett JJ, Schwarzacher W (2005) Surf Sci 576:212
18. Lucas I, Perez L, Aroca C, Sanchez P, Lopez E, Sanchez MC (2005) J Magn Magn Mater 290–291:1513
19. Choi P, Silva MD, Klement U, Al-Kassab T, Kirchheim R (2005) Acta Materialia 53:4473
20. Emerson RN, Kennady CJ, Ganesan S (1006) J Appl Sci 6:227
21. Hamid ZA (2003) Mater Lett 57:2558
22. Ibrahim MAM, Rehim SSA, Moussa SO (2003) J Appl Electrochem 33:627
23. Dulal SMSI, Yun HJ, Shin CB, Kim C-K (2007) J Electrochem Soc 154:D494
24. Dulal SMSI, Charles EA, Roy S (2004) Electrochim Acta 49:2041
25. Ying RY (1988) J Electrochem Soc 135:2957
26. Ishikawa M, Enomoto H, Matsuoka M, Iwakura C (1995) Electrochim Acta 40:1663
27. Dulal SMSI, Charles EA (2007) J Alloys Compd (in press) doi: 10.1016/j.jallcom.2007.01.020
28. Dulal SMSI, Charles EA, Roy S (2004) J Appl Electrochem 34:151
29. Armyanov S, Volova E, Franquet A, Dille J, Delplancke J-L, Hubin A, Steenhaut O, Kovacheva D, Tatchev D, Vassilev DT (2005) J Electrochem Soc 152:C612