

Research on NiCoB Diffusion Barrier Film Prepared by Electroless Deposition for ULSI-Cu Metallization

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Abstract. In this paper, NiCoB/Cu/NiCoB/Si and NiCoB/Si samples were prepared by electroless deposition. XPS, XRD, FPP and AFM were used to characterize the elemental valence and composition, phases, sheet resistance and surface morphology of the samples. According to the results, it can be found that the electroless deposited NiCoB film was amorphous, and it was composed of CoB compound and elementary Ni. The results of NiCoB films annealed at temperatures ranging from 500°C to 850°C demonstrated that the electroless deposited NiCoB film can block Cu diffusion effectively until 850°C.

1. Introduction

Admittedly, the resistance-capacitance delay of a circuit has become the limiting factor in the speed of device with the decrease in the minimum feature size of ultra-large scale integration [1-4]. In order to resolve the crisis caused by the interconnection delay, Cu has been applied as the interconnect material due to its low resistivity and high resistance to electromigration [5-8]. However, there must be an ideal barrier layer between Cu and Si due to the poor adhesion of Cu as well as the diffusion between Cu and Si [9].

Owing to the high melting point, small contact resistance, low stress and excellent thermostability, Ti alloy and Ta alloy became the most widely used diffusion barrier materials in Cu metallization as well as in Al based metallization [10-13]. Recently, with the continuous improvement of integration, traditional Ti alloy and Ta alloy barrier layers were no longer qualified for the job in terms of the film thickness, thermostability, electrical conductivity and uniformity. Besides, it is an arduous task to explore barrier layer materials with superior performance.

In comparison with other physical and chemical vapor deposition methods, electroless deposition is a promising technique because of the relative low temperature, low cost, low defect density, high uniformity and conformality [14-16]. In most cases, electroless deposition of diffusion barrier materials concentrated in cobalt and nickel based alloys [17, 18]. Sung-Te Chen [19] etc. studied the Co-P barrier film and found that the Co-P barrier layer not only acted as catalysts for the electroless deposition of the copper film, but also increased the thermostability of the Cu metallization layer. Hila Einati [20] et al. found that the Co-W-B film with 2.2 at% boron revealed the high resistance to

air oxidation. S.M.S.I. Dulal [21] etc invented an alkali-metal-free bath for electroless deposition of Co-W-P film for copper interconnections. A. Kohn [15] et al. pointed out that the increase of W degraded the quality of Co-W-P alloy film. Anuj Kumar [22] etc discovered the Ni-Co-P film, with lower Co and higher P contents can prevent the diffusion of Cu until 500 °C. N-dimethyl amine borane (DMAB) can be used as reducing agent in electroless Ni, Ni baths with DMAB can work in both acid and alkaline baths, and the overall reduction reactions produce metallic nickel or nickel boride [23]. DMAB can reduce Ni^{2+} and Co^{2+} from solution at the same time to co-deposit Ni-Co-B alloy [24]. Besides, Ni-Co-B film possesses excellent magnetic property and corrosion resistance [25-27], it has been widely used in the thin magnetic recording media and catalysis material [25, 28], yet few studies have been conducted on the NiCoB barrier layer film on Cu interconnection. As a result, it is a great interest to investigate how a NiCoB alloy film can be used as a diffusion barrier layer on Cu interconnections.

In this study, NiCoB films were deposited as a barrier layer against Cu diffusion based on the above mentioned electroless technique. NiCoB/Si and NiCoB/Cu/NiCoB/Si samples were prepared and researched in order to obtain the NiCoB film with excellent barrier property.

2. Experimental

The substrates used in this study were single crystal n-type (100) silicon with the resistivity of 1~10 Ω -cm. Prior to electroless deposition, the Si substrates were pre-treated as follows. At first, the wafer was ultrasonically cleaned for 20 min in absolute alcohol. Then, it was treated a second time in an ultrasonic assisted bath containing a roughening solution (4% H_2SO_4 + 5% H_2O_2) for 20 min followed a sensitization process for 5 min in SnCl_2 +HCl solution (20 g/l $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 40 ml/l HCl). The cleaned wafer was subjected to ultrasonic treatment for 20 min in palladium activating solution (0.25 g/l PdCl_2 + 10 ml/l HCl + 3.2 g/l $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ + 0.5 g/l $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ + 250 g/l NaCl + 50 g/l urea). Finally, it is the peptization process for 40 s in 10% HCl solution in a 45°C water bath.

Electroless deposition was conducted immediately after the pretreatment of Si substrates. The experimental condition and composition of NiCoB as well as Cu plating baths are given in Table 1. Deposition time for the first film (NiCoB), the second film (Cu) and the third film (NiCoB) was 5 min, 2 min, 30 s respectively. In addition, the deposition time for the single NiCoB film was also 5 min.

NiCoB/Si and NiCoB/Cu/NiCoB/Si samples were annealed at 500°C ~850 °C for 30 min in an argon atmosphere. XPS, XRD, FPP and AFM were used to characterize the elemental valence and composition, phases, sheet resistance and surface morphology of these samples before and after annealing.

3. Results and Discussion

The thickness of films was measured by the SGC-10 film thickness gauge, the first film (NiCoB barrier layer) is 40 nm, the second film (Cu) was 20 nm and the third film (NiCoB) was 50 nm. The other characterizations of the deposited NiCoB/Si and NiCoB/Cu/NiCoB/Si samples are given as follows.

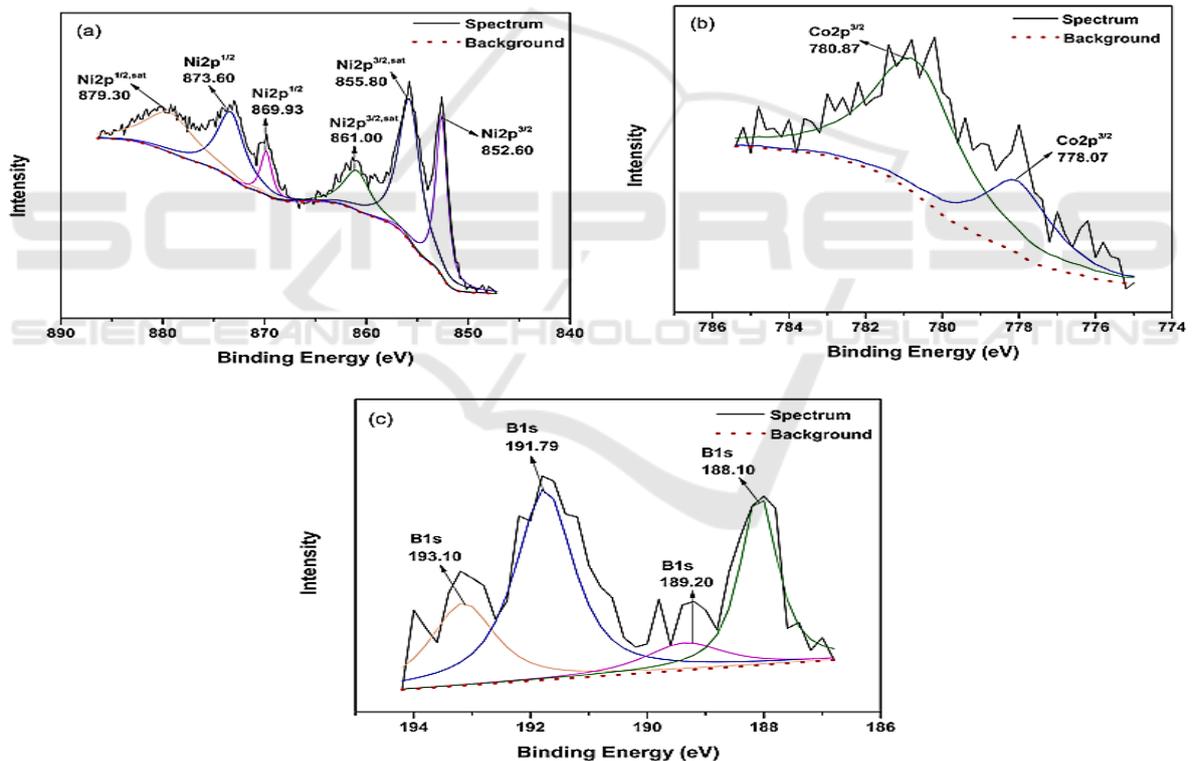
3.1. Analysis of elemental valence state and composition

The elemental valence of the NiCoB film was determined from the element spectra as shown in Figure1.

As shown the Figure 1(a), the bonding of Ni emerged at 869.93 eV and 852.60 eV respectively, indicating that Ni element existed in the form of elementary Ni in the electroless deposited NiCoB film. In addition, the bonding of Ni-O appeared at 879.30 eV, 873.60 eV, 861.00 eV and 855.80 eV, which corresponds to NiO, indicating that a small amount of NiCoB film on the surface has been oxidized.

Table 1. Experimental conditions and composition of the plating baths for electroless deposition of NiCoB and Cu.

	Sample names	Concentration (g/l)	Operating conditions
NiCoB	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	41.17	pH: 11 Temperature: 85 °C
	$\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$	14.11	
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	28.91	
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	8.43	
	DMAB($\text{C}_2\text{H}_{10}\text{BN}$)	2.35	
	$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	15	
	NH_4F	1.0	
Cu	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	20	pH: 12 Temperature: 77.5 °C
	EDTA-2Na	39	
	$\text{CHOCOOH} \cdot \text{H}_2\text{O}$	13.8	
	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	21	
	α - α' bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$)	0.01	


Figure 1. Element spectra of Ni2p (a), Co2p (b) and B1s (c).

In the Co2p spectrum, the bonding of Co-O and Co-B appeared at the 780.87 eV and 778.07 eV, the corresponding substances were CoO and CoB. It can be inferred that the Co element in the electroless deposited NiCoB film primarily existed in CoB. Figure 1(c) is the spectrum of B1s, in which the bonding of Co-B can be observed at 188.10 eV. In addition, a B_6O peak (189.20 eV) and B_2O_3 peaks (193.10 eV, 191.79 eV) emerged, which resulted from the oxidation of the exterior

NiCoB film. XPS analysis demonstrated that the electroless deposited NiCoB film was mainly composed of CoB compound and elementary Ni.

3.2. Analysis of phase

Figure 2 shows the XRD patterns of NiCoB/Si before and after annealing at 500 °C~850 °C. As shown in this figure, the unannealed samples were almost amorphous. After annealing the film from 500 °C to 800 °C, the film was crystallized and there were some new phases formed and disappeared constantly. Annealing the film at 850 °C, phase species of the film were much more than that of other annealing temperatures, indicating that the effect of heat treatment on the phase changes of NiCoB film is of much significance. The concentration of Ar was 99.99%, leading to the appearance of Co_2SiO_4 and $\text{Co}_3(\text{BO}_3)_2$, trace of oxygen in Ar reacted with NiCoB film and Si substrate during the annealing process.

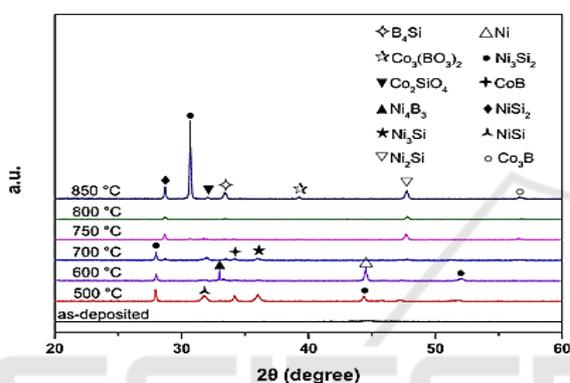


Figure 2. XRD patterns of NiCoB/Si samples before and after annealing.

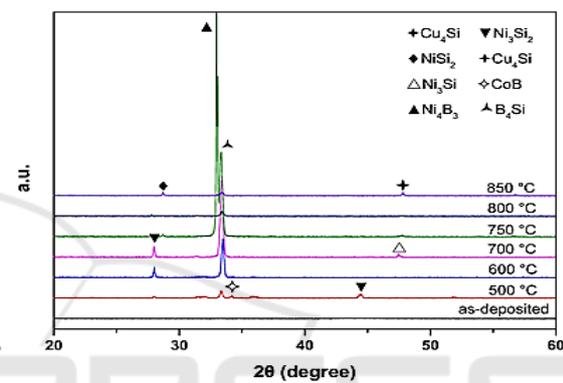


Figure 3. XRD patterns of NiCoB/Cu/NiCoB/Si samples before and after annealing.

Figure 3 is the XRD patterns of NiCoB/Cu/NiCoB/Si before and after annealing at 500 °C~850 °C. As shown in Figure 3, the electroless deposited multilayer film was amorphous. After annealing from 500 °C to 800 °C, the film was crystallized and some new phases formed and then disappeared. Ni was prone to interstitial diffusion in Si and filled the atomic gap, this led to the formation of Ni-Si compounds after annealing. There were also CoB or B_4Si appeared after annealing, CoB and B_4Si may form a segregation layer between NiCoB and Cu, NiCoB and Si, so there was no diffusion of Cu occurred. When the annealing temperature was 850 °C, there was a Cu_4Si diffraction peak present, indicating that the barrier property of the NiCoB film failed completely and Cu diffusion occurred.

3.3. Analysis of sheet resistance

The change in the sheet resistance of deposited samples in dependence on the annealing temperature is presented in Figure 4. Sheet resistance of unannealed NiCoB/Si sample was $4.591 \Omega/\square$, so the resistivity of NiCoB film was $18.364 \mu\Omega \cdot \text{cm}$. After annealing the film at 500 °C, the sheet resistance decreased to $0.967 \Omega/\square$. On one hand, there were some new Ni-Si compounds after annealing, which have lower sheet resistance, and the defect density decreased after annealing. On the other hand, the Si wafer resistance also had an effect on the sheet resistance of NiCoB film. Then the sheet resistance increased to $1.452 \Omega/\square$ for an annealing up to 850 °C, which may be caused by the changes of phase and structure of NiCoB film. Especially after 850 °C annealing, too many kinds of phases produced more grain boundaries. The sheet resistance of unannealed NiCoB/Cu/NiCoB/Si sample was $1.935 \Omega/\square$ and it was smaller than that of unannealed NiCoB/Si sample. Average dislocation density of

multilayer film was lower than that of monolayer film, the effect of defects on electron scattering weakened, it may cause a lower resistance. Moreover, the Cu wafer resistance also had an effect on the sheet resistance of the surface NiCoB film. Annealing the film from 500 °C to 700 °C, sheet resistance of this film decreased to 0.899 Ω/\square followed by an increase to 6.724 Ω/\square for an annealing up to 800 °C. However, it increased sharply after annealing at 850°C. In combination with the results of XRD analysis, the increase of sheet resistance was due to the formation of highly resistive Cu₄Si. Therefore, analysis about sheet resistance suggested that the complete failure temperature of the NiCoB barrier film in Cu interconnections is 850°C.

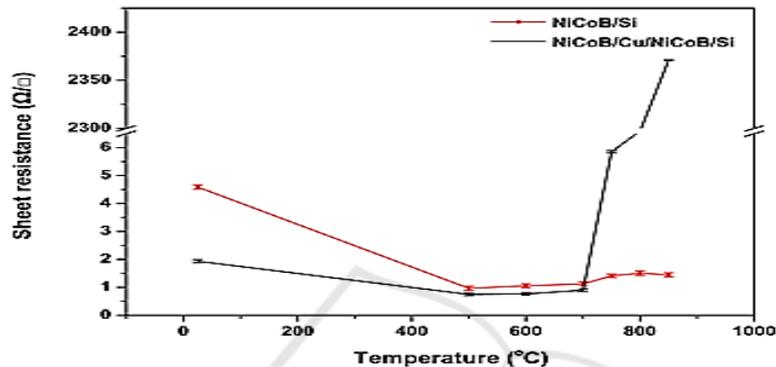


Figure 4. Variation of sheet resistance of NiCoB/Si and NiCoB/Cu/NiCoB/Si samples with temperature.

Table 2 lists some electroless deposited diffusion barrier layer films of ternary system [22, 29-32]. Compared to these diffusion barrier layers, NiCoB film has a low resistivity and excellent thermostability, so it is very promising to be applied to barrier layer.

Table 2. Electroless deposited diffusion barrier layer films and its performance [22, 29-32].

Diffusion barrier layer film	Thickness (nm)	Resistivity ($\mu\Omega\cdot\text{cm}$)	Failuer temperature (°C)	Reference
NiCoP	50	109	500	[22]
CoWP	30	80	500	[29]
NiMoP	15~20	80	700	[30]
NiMoB	40	94	500	[31]
CoMoB	30	127.5	600	[32]
NiCoB	40	18.364	850	This work

3.4. Characterization of surface morphology

Through using atomic force microscopy, surface morphologies of the electroless deposited NiCoB/Si samples and the NiCoB/Cu/NiCoB/Si samples before and after annealing from 500 °C to 850 °C were analyzed.

As shown in Figure 5(a) and Figure 5(b), the surface of deposited NiCoB/Si and NiCoB/Cu/NiCoB/Si films presented "orange peel". It can be inferred that the presence of Cu in the film stuck affected the surface morphology.

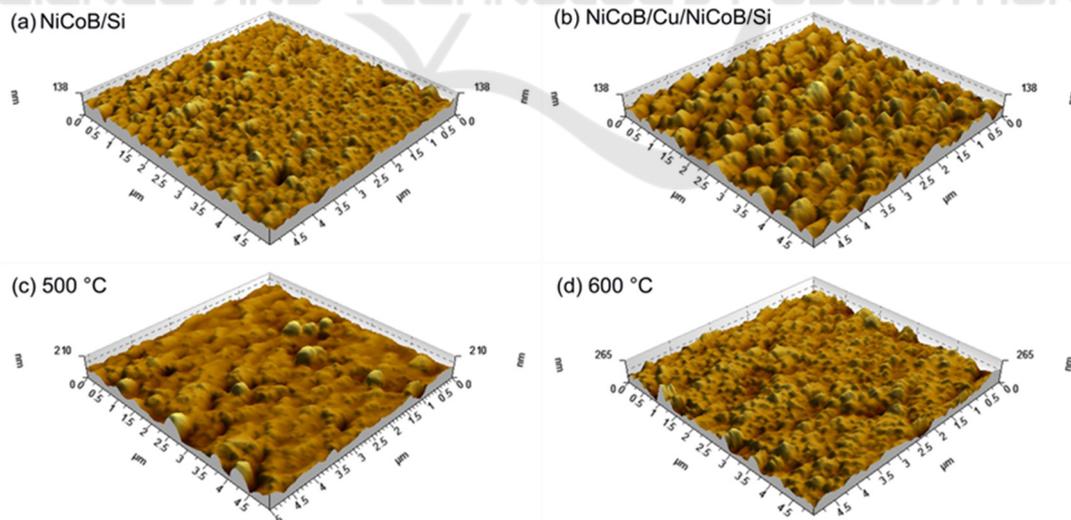
The surface morphologies of annealed NiCoB/Cu/NiCoB/Si samples were shown from Figure 5(c) to Figure 5(h). The surface of the NiCoB/Cu/NiCoB/Si film roughened after 500°C annealing.

Compared with the XRD data of Figure 3, it can be concluded that the morphological change occurred result from the development of new phases in the film, specifically Ni_3Si_2 , B_4Si , and CoB . Annealing the NiCoB/Cu/NiCoB/Si film at 600°C , the overall grains were more uniform distribution and uneven, besides, a few isolated larger grains, resulting in much larger roughness. There was an apparent aggregation of small grains after 700°C annealing and it was a stage that new phases were generating in, such as Ni_3Si , Ni_3Si_2 and B_4Si . After annealing at 750°C , large grains led to a larger roughness. Some grains connected each other and appeared island-growth after 800°C annealing, surface became smoother and the surface energy decreased. Yet annealing at 850°C caused the development of small grains on the surface of the original grains. With overall consideration of XRD, AFM and sheet resistance data, the complete failure temperature of the NiCoB barrier film in Cu interconnections is 850°C . The failure mechanism is that after annealing at 850°C , new phases of NiSi_2 , Ni_4B_3 , and B_4Si were appeared and accompanied by a large number of grain boundaries. Cu diffused across these grain boundaries and reacted with Si -substrate. Formation of highly resistive Cu_4Si , causing the changes of surface morphologies and sheet resistance of NiCoB/Cu/NiCoB/Si samples.

4. Conclusions

In this paper, NiCoB thin films were deposited by electroless deposition as single layers and as diffusion barrier layers on Cu interconnections. XRD and XPS analyses demonstrated that the electroless deposited NiCoB film was amorphous and it was composed of CoB compound and elementary Ni . According to annealing experiments, it can be found that the failure temperature at which Cu diffusion occurred was 850°C . After 850°C annealing, NiCoB barrier layer was crystallized and grain boundaries provided channels for the diffusion of copper. Reaction between Cu and Si -substrate resulted in the formation of Cu_4Si which had high resistivity.

According to our study, the electroless deposited NiCoB thin film has a great promising to be applied to diffusion barrier layer for Cu interconnections because of its excellent adhesion, low resistivity and high failure temperature.



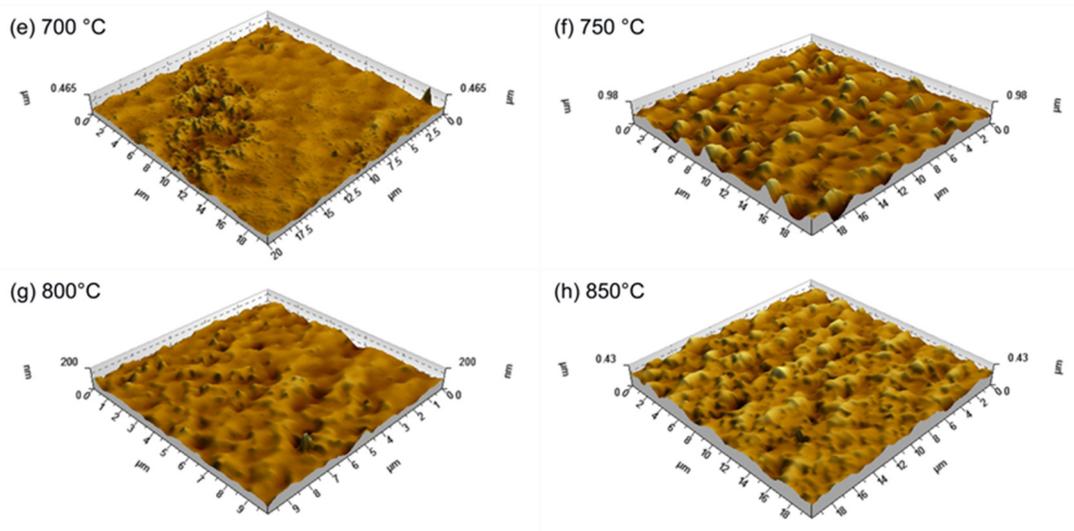


Figure 5. AFM surface morphologies of unannealed NiCoB(a) and NiCoB/Cu/NiCoB/Si (b) samples and NiCoB/Cu/NiCoB/Si samples annealed at different temperatures((c)~(h)).

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Reference

- [1] Hu C K and Harper J M E 1998 Copper interconnections and reliability *Materials Chemistry and Physics* 52 5-16
- [2] Murarka S P 1997 Advanced materials for future interconnections of the future need and strategy *Microelectronic Engineering* 37/38 29-37
- [3] Wong H Y, Mohd Shukor N F and Amin N 2007 Prospective development in diffusion barrier layers for copper metallization in LSI *Microelectronics Journal* 38 777-782
- [4] Yang J Y, Hong R T and Huang M J 2005 A comparative molecular dynamics study of copper trench fill properties between Ta and Ti barrier layers *Materials Science in Semiconductor Processing* 8 622-629
- [5] Ofek Almog R, Sverdlov Y, Goldfarb I and Shacham-Diamand Y 2007 CoWBP capping barrier layer for sub 90 nm Cu interconnects *Microelectronic Engineering* 84 2450-2454
- [6] Lin L W, Liu B, Ren D, Zhan C Y, Jiao G H and Xu K W 2013 Effect of sputtering bias voltage on the structure and properties of Zr-Ge-N diffusion barrier films *Surface and Coatings Technology* 228 S237-S240
- [7] Dai X H, Zhang L, Feng Z D, Li X H, Guo J X, Fu Y J, Zhou Y, Zhao Q X, Lou J Z, Ma L X, Zhang X Y and Liu B T 2015 Barrier performance of ultrathin amorphous Nb-Ni film between copper and silicon *Materials Letters* 159 94-97
- [8] Lee H J, Hong T E and Kim S H 2016 Atomic layer deposited self-forming Ru-Mn diffusion barrier for seedless Cu interconnects *Journal of Alloys and Compounds* 686 1025-1031
- [9] Sharma S, Kumara M, Rani S, Kumar D and Tripathi C C 2016 Structural and electrical characterization of CoNiO monolayer as copper diffusion barrier in integrated circuits *Materials Science in Semiconductor Processing* 48 1-8
- [10] Rha S K, Lee W J, Lee S Y, Hwang Y S, Lee Y J, Kim D I, Kim D W, Chun S S and Park C O 1998 Improved TiN film as a diffusion barrier between copper and silicon, *Thin Solid*

- Films. 320 134-140
- [11] Burgess S R, Donohue H, Buchanan K, Rimmer N and Rich P 2002 Valuation of Ta and TaN-based Cu diffusion barriers deposited by Advanced Hi-Fill (AHF) sputtering onto blanket wafers and high aspect ratio structures *Microelectronic Engineering* 64 307-313
- [12] Jang S Y, Lee S M and Baik H K 1996 Tantalum and niobium as a diffusion barrier between copper and silicon *Journal of Materials Science: Materials in Electronics* 7 271-278
- [13] Wang W L, Peng K T, Kuo H C, Yeh M H, Chien H J and Ying T H 2014 The contact resistance reduction of Cu interconnects by optimizing the crystal behavior of Ta/TaN diffusion barrier *Materials Science in Semiconductor Processing* 27 860-864
- [14] Shacham-Diamand Y, Osaka T, Okinaka Y, Sugiyama A and Dubin V 2015 30 years of electroless plating for semiconductor and polymer micro-systems *Microelectronic Engineering* 132 35-45
- [15] Kohn A, Eizenberg M and Shacham-Diamand Y 2003 The role of microstructure in nanocrystalline conformal Co_{0.9}W_{0.02}P_{0.08} diffusion barriers for copper metallization *Applied Surface Science* 212-213 367-372
- [16] Aithal R K, Yenamandra S, Gunasekaran R A, Coane P and Varahramyan K 2006 Electroless copper deposition on silicon with titanium seed layer, *Materials Chemistry and Physics* 98 95-102
- [17] Hamid Z A, Aal A A, Shaaban A and Hassan H B 2009 Electrodeposition of CoMoP thin film as diffusion barrier layer for ULSI applications *Surface and Coatings Technology* 203 3692-3700
- [18] Tarozaitė R, Sukackienė Z, Sudavičius A, Juškėnas R, Selskis A, Jagminienė A and Norkus E 2009 Application of glycine containing solutions for electroless deposition of Co-P and Co-W-P films and their behavior as barrier layers *Materials Chemistry and Physics* 117 117-124
- [19] Chen S T, Liu Y Y and Chen G S 2015 Ultrathin cobalt-alloyed barrier layers for copper metallization by a new seeding and electroless-deposition process *Applied Surface Science* 354 144-147
- [20] Einati H, Bogush V, Sverdlov Y, Rosenberg Y and Diamand Y S 2005 The effect of tungsten and boron on the Cu barrier and oxidation properties of thin electroless cobalt-tungsten-boron films *Microelectronic Engineering* 82 623-628
- [21] Dulal S M S I, Kim T H, Rhee H, Sung J Y and Kim C K 2009 Development of an alkali-metal-free bath for electroless deposition of Co-W-P capping layers for copper interconnections *Journal of Alloys and Compounds* 467 370-375
- [22] Kumar A, Kumar M K and Kumar D 2012 Effect of composition on electroless deposited Ni-Co-P alloy thin films as a diffusion barrier for copper metallization *Applied Surface Science* 258 7962-7967
- [23] Sudagar J, Lian J S and Sha W 2013 Electroless nickel, alloy, composite and nano coatings-A critical review *Journal of Alloys and Compounds* 571 183-204
- [24] Saito T, Sato E, Matsuoka M and Iwakura C 1998 Electroless deposition of Ni-B, Co-B and Ni-Co-B alloys using dimethylamineborane as a reducing agent *Journal of Applied Electrochemistry* 28 559-563
- [25] Wang S L 2007 Electroless deposition of Ni-Co-B alloy films and influence of heat treatment on the structure and the magnetic performances of the film *Thin Solid Films* 515 8419-8423
- [26] Narayanan T S N S, Stephan A and Guruskanthan S 2004 Electroless Ni-Co-B ternary alloy deposits: preparation and characteristics *Surface and Coatings Technology* 179 56-62
- [27] Gamboa S A, Gonzalez-Rodriguez J G, Valenzuela E, Campillo B, Sebastian P J and Reyes-Rojas A 2006 Evaluation of the corrosion resistance of Ni-Co-B coatings in simulated PEMFC environment *Electrochimica Acta* 51 4045-4051

- [28] Wang H M, Yu Z B, Chen H Y, Yang J and Deng J F 1995 High activity ultrafine Ni-Co-B amorphous alloy powder for the hydrogenation of benzene *Applied Catalysis A: General* 129 L143-L149
- [29] Kohn A, Eizenberg M, Shacham-Diamand Y, Israel B and Sverdlov Y 2001 Evaluation of electroless deposited Co (W,P) thin films as diffusion barriers for copper metallization *Microelectronic Engineering* 55 297-303
- [30] Chou Y H, Sung Y, Liu Y M, Pu N W and Ger M D 2009 Amorphous Ni-Mo-P diffusion barrier deposited by non-isothermal deposition *Surface and Coatings Technology* 203 1020-1026
- [31] Wang Y C, Chen X H, Ma W H, Liu X M, Li Y P, Bi P and Xiang F W 2017 Electroless Deposition of NiMoB Diffusion Barrier Layer Film for ULSI-Cu Metallization *Key Engineering Materials* 727 900-906
- [32] Liu X M, Chen X H, Ma W H, Li Y P, Bi P, Wang Y C and Xiang F W 2016 Electroless CoMoB Diffusion Barrier Layer for ULSI-Cu Metallization *Materials Science Forum* 847 91-96

