Electroplating of Au-Ni and Au-Co Alloy Films

A. He, Q. Liu and D. G. Ivey[*]
Department of Chemical and Materials Engineering
University of Alberta
Edmonton, Alberta, Canada

In this work, two non-toxic hard gold plating solutions have been developed. The plating solutions are prepared by adding nickelous chloride hexahydrate or cobaltous sulfate heptahydrate into pure gold plating solutions. The two solutions are environmentally benign, easy to prepare, easy to control and electrodeposition can be done at room temperature. The plated films have hardness values of 80 to 150 VHN for Au-Ni films and 88 to 130 VHN for Au-Co films. The plating rates are about 10 µm per hour when a current density of 4.0 mA/cm^2 is applied. Au-Ni solutions can be used for up to two weeks after preparation, giving reproducible deposits in terms of composition and morphology. For Au-Co plating, solution lifetime can be extended to more than three weeks by reducing the electrodeposition current density to 3.0 mA/cm^2 (instead of 4.0 mA/cm^2).

Keywords: *Au-Ni/Au-Co films, electroplating, non-toxic solutions, ammonium citrate, sodium sulfite.*

Introduction

Electroplated Au-Ni or Au-Co films are generally referred to as hard gold films, since their hardness values are much higher than those of pure gold films.[1-3] Unlike pure gold films, which are mainly used for decorative purposes, when used in semiconductor metallizations or in Au-Sn alloy films for optoelectronic and MEMS packaging, hard gold films are mainly employed as contact surfaces (*e.g.*, in multiple-insertion electrical contacts found on printed wiring board contacts or spring contacts) where wear resistance, corrosion resistance and good lubrication are needed. Typically, the thicknesses of the top coatings on contacts are about 0.8 to 2.5 µm. The addition of a small amount (0.3 to 1.6 at%) of alloying elements such as cobalt, nickel or palladium can increase the hardness from 40 to 60 VHN for pure gold to the 80 to 200 VHN range.[1] Traditionally, hard gold films are electroplated with cyanide-based baths.[1,4-7] Obviously, such electroplating solutions are not environmentally friendly. A non-cyanide hard gold plating solution has recently been reported by Gun and Podlaha.[8] This solution contains no cyanide component, as it is prepared based on a commercial formulation.[**] However, this solution contains a toxic element, arsenic, making it environmentally hazardous.

In our studies of pure gold electroplating, we have developed an environmentally friendly electroplating solution, which contains neither cyanide nor arsenic components.[9] The present work is a continuation of the gold work and focuses on the development of hard gold plating solutions by adding metallic ions, such as nickel or cobalt ions.

Experimental

The chemicals used were reagent grade potassium aurichloride ($KAuCl_4$, molecular weight (MW) = 377.88 g/mol), tri-ammonium citrate ($HOC(CO_2NH_4)(CH_2CO_2NH_4)_2$, MW = 243.22 g/mol), sodium sulfite (Na_2SO_3, MW = 126.04 g/mol), nickelous chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, MW = 237.71 g/mol, hereafter referred to as nickelous chloride) and cobaltous sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$, MW = 281.10 g/mol, hereafter referred to as cobaltous sulfate). Nickelous chloride provides the nickelous ions and cobaltous sulfate provides the cobaltous ions.

The first step was to prepare a pure gold plating solution. The procedure is given in detail in previous work[9] and is summarized here. The tri-ammonium citrate was dissolved in de-ionized water, followed by the addition of $KAuCl_4$ salt. The solution was stirred until the $KAuCl_4$ salt was fully dissolved. This solution was initially transparent with a brownish color; after about 5 min, the solution became more opaque, similar in appearance to mud. The opaque solution became transparent again after the addition of Na_2SO_3, and turned to a golden color, which was followed by a gradual transition (over a period of ~45 min) to a faint yellowish color. This solution was then ready for pure gold plating or as a precursor for producing a hard gold plating bath. Starting from this precursor, nickelous chloride or cobaltous sulfate was added and

---

[*] *Corresponding author:*
Dr. Douglas Ivey
536 Chemical/Materials Engineering Building
Edmonton, Alberta, Canada T6G 2G6
Phone: (780) 492-2957
E-mail: doug.ivey@ualberta.ca

[**] *Techni Gold 25 E, Technic, Inc., Cranston, RI.*

the resultant solution was stirred until the salts were completely dissolved. The solution was then ready to electroplate hard gold films. The solution was green when nickelous chloride was added and pink when cobaltous sulfate was added. Both hard gold plating solutions were transparent. All electroplating processes in this work were carried out at room temperature.

The electroplating cell consisted of two electrodes: platinum as the non-consumable anode and a metallized silicon wafer piece as the cathode. Silicon wafers with a thickness of 0.5 mm were metallized with titanium (~50 nm) as an adhesion layer, followed by gold (~300 nm) or platinum (~50 nm) as a seed layer for the electrodeposition. Both metal layers were deposited by magnetron sputtering. Pulsed current plating was utilized (Dynatronix DuPR10-.1-.3 power supply), with average current densities ranging from 1.0 to 6.0 mA/cm^2 and a duty cycle of 10 msec (2 msec on and 8 msec off).

The morphologies and compositions of the electroplated films were characterized using scanning electron microscopy (SEM), with a Hitachi H2700 SEM equipped with an ultra thin window (UTW) energy dispersive x-ray (EDX) detector operating at 20 kV. The distribution of the nickel or cobalt throughout the electroplated film thickness was examined using secondary ion mass spectrometry (SIMS) depth profiling, with an ION-TOF SIMS IV operated with an analysis source of gallium at 15 kV and a beam current of 2.5 pA, and an oxygen sputtering source at 1.0 kV and a beam current of 80 nA. Hardness measurements were carried out on an HP100 XYp micro-indentation probe (Fischer Technology, Inc.). The thickness of the electrodeposited films for hardness measurements was about 40 μm. The selected indentation load was 25 mN. The load application time and the unloading time were 20 sec in both cases. Using this load, the indentation depth was less than one-tenth of the thickness of the plated films. As such, the measured hardness values were not affected by the underlying substrate.

Results and discussion

Electroplating of Au-Ni alloys

Molar ratios in the range of 0.11 to 3.18 for $NiCl_2 \cdot 6H_2O/KAuCl_4$ were tested for Au-Ni plating. Table 1 gives the compositions of solutions studied in this work. The pH values of the solutions were around 6.5. Solution I was selected initially to test the viability of plating after adding the fourth component (nickelous chloride) to the pure gold plating solution. The solution color changed from a faint yellow to green after addition of the nickelous chloride. The compositions of Solutions II thru V were selected to adjust the solution concentrations according to the electroplating results from Solution I. For Solution I, current densities between 1.0 and 6.0 mA/cm^2 were applied for electrodeposition. SEM images showed that all electroplated films were smooth if the films were plated at a current density of 4.0 mA/cm^2 or lower, and rough above 4.0 mA/cm^2. Figure 1 shows several examples.

Figures 1a and 1b show SEM cross-section and plan view images from a film plated at 4.0 mA/cm^2, and Figs. 1c and 1d show images from a film plated at 6.0 mA/cm^2. The film in Figs. 1a and 1b is smooth and has fine grains, while the film in Figs. 1c and 1d is very rough and discontinuous at some locations. The successful plating of the films with current density equal to or less than 4.0 mA/cm^2 implies that there is potential to develop this electrolyte into a hard gold plating solution.

The addition of nickelous chloride does not deteriorate the pure gold solution, although the solution color is changed from faint yellow to green. EDX measurements of the deposits show that the nickel concentration in the films electrodeposited from Solution I at current densities $\leq$ 4.0 mA/cm^2 is about 0.1 to 0.2 at%, which is lower than the composition range (0.3 to 1.6 at%) of deposits reported in Reference 1. SEM observations show that, although the nickelous chloride concentration in Solution II was doubled compared with Solution I, the morphologies of deposits from Solution II show similar results to those from Solution I, and the nickel compositions in the plated films have not dramatically increased. Further increases in the nickelous chloride concentration to 0.105M (Solution III, which is almost eight times higher than the nickelous chloride concentration in Solution I) and 0.140M (Solution IV, which has ten times the nickelous chloride concentration of Solution I) still allowed films to be electrodeposited.

It is interesting to note that 4.0 mA/cm^2 still appears to be a critical current density for plating. The deposited film is smooth if plated at this current density and the plated film becomes rough if plated at current densities greater than 4.0 mA/cm^2. This observation implies that the addition of nickelous chloride does not change the plating process very much. In fact, the plating rate for Au-Ni films from Solutions III and IV is still about 10 μm per hour, which is similar to the rate for pure gold from a gold plating solution.[9]

Table 1

Au-Ni plating solutions studied in this work

Solution	Tri-ammonium Citrate, mol/L	$KAuCl_4$, mol/L	Na_2SO_3, mol/L	$NiCl_2 \cdot 6H_2O$ mol/L
I	0.411	0.066	0.563	0.014
II	0.411	0.066	0.563	0.042
III	0.411	0.066	0.563	0.105
IV	0.411	0.066	0.563	0.140
V	0.411	0.066	0.563	0.210

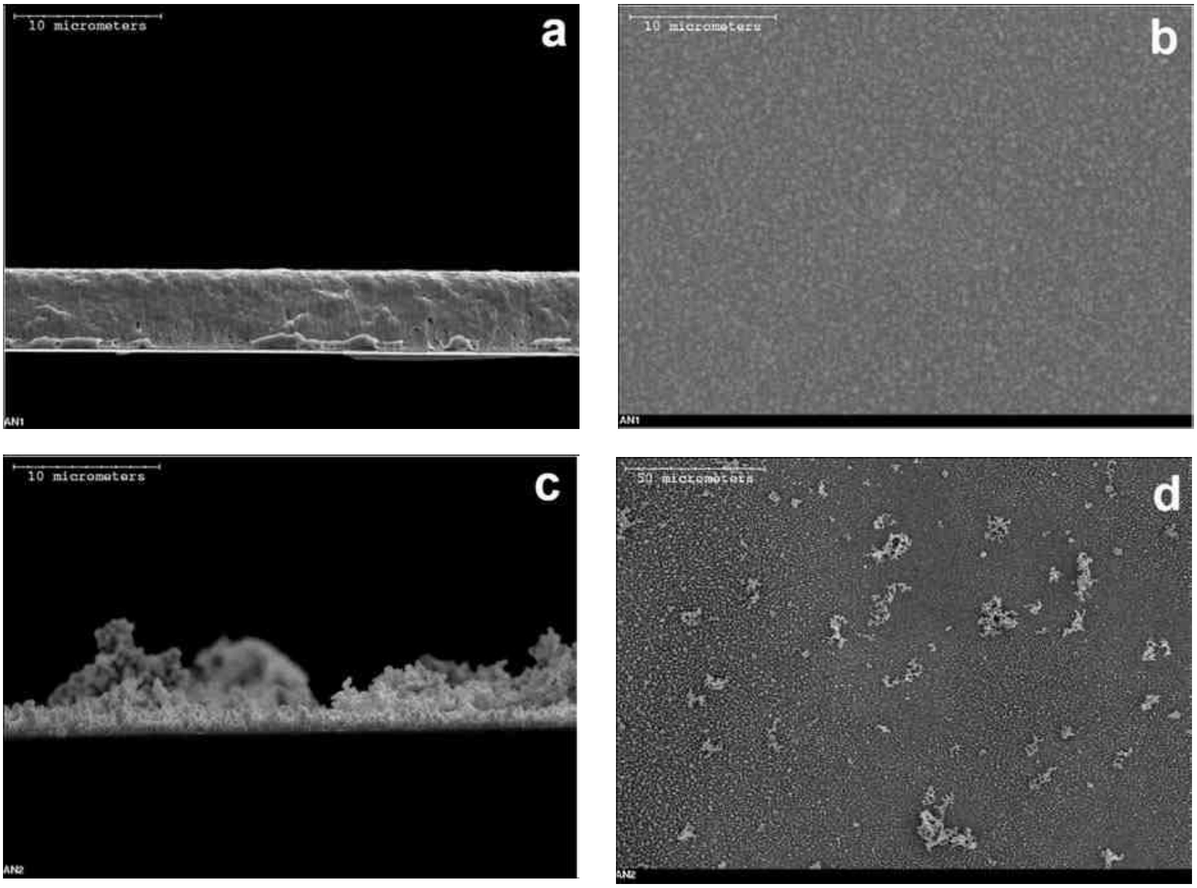

Figure 1—*SEM cross-section and plan view images showing Au-Ni films electrodeposited from Solution I for 30 min at current densities of (a) and (b); 4.0 mA/cm²; (c) and (d), 6.0 mA/cm².*

Composition analysis shows that films plated at a current density of 4.0 mA/cm² have nickel concentrations of ~0.8 at% from Solution III and ~1.3 at% from Solution IV. Figures 2a and 2b show typical SEM images for deposited films from Solution III and Figs. 2c and 2d show images of films from Solution IV. Both the cross-sectional and plan view images show that the plated films are smooth. The films are even smoother if electrodeposited at lower current densities of 2.5 or 3.0 mA/cm². For these current densities, the films still have nickel concentrations of 0.5 at% or higher. However, the plating rates are lower at lower current densities.

Increasing the nickelous chloride concentration in the electroplating solutions has two side effects on the plating process. On one hand, increasing the amount of nickelous chloride increases the nickel concentration in the plated films, which is desirable for hard gold plating. On the other hand, the higher amount of nickelous chloride increases stress in the electrodeposited films. Cracking is induced when the nickelous chloride in the plating solution reaches a concentration of 0.210M (Solution V, which is about 15 times the nickelous chloride concentration in Solution I). Figure 3 shows an example. Figure 3a shows an SEM plan view image of a film plated from Solution V at 2.0 mA/cm² and clearly shows that the film has large cracks (as indicated by the arrows) and part of the film has rolled up. EDX spectra from Fig. 3a are shown in Figs. 3b and 3c, respectively. Figure 3b is from an area where the film is continuous and crack-free (marked with the letter "B"). The composition of this area is ~7.1 at% Ni. Figure 3c is from the region under the rolled-up film (marked with the letter "C") and clearly reveals that this area is only the silicon substrate. The presence of cracks and film delamination indicates that the film stress is sufficient to remove the seed layer as well as the titanium adhesion layer. The internal stress in the plated film is even higher as the current density increases, as shown in Fig. 3d (plated at a current density of 3.0 mA/cm²) and 3e (plated at a current density of 4.0 mA/cm²). In both cases, most of the film has delaminated and either folded or rolled up. It should be noted that the scale bars in Figs. 3a, 3d and 3e are either 500 or 600 μm, so that the cracks and rolled-up films are on the macro scale.

From the phase diagram,[10] it is apparent that the Au-Ni system forms a solid solution with solubility over the entire composition range, so that an Au-Ni film with ~7 at% Ni should not generate cracks or delaminate if it is fabricated using traditional metallurgical techniques, since both gold and nickel are ductile metals. For practical applications, higher nickelous chloride concentrations in solution are not recommended, unless the plating process is carried out at higher temperatures, since higher temperatures can reduce internal stress.[11] However, higher temperature electroplating can also increase the average grain sizes of electrodeposited films,[12] which can reduce their hardness. In addition, higher temperature plating adds complexity to the plating process. Considering all these aspects, it is suggested that hard Au-Ni film plating should be carried out with Solution III or Solution IV at room temperature.

In order to examine the composition of nickel through the film thickness, depth profiling was carried out on a deposit obtained from Solution V using SIMS (Fig. 4). The nickel is distributed

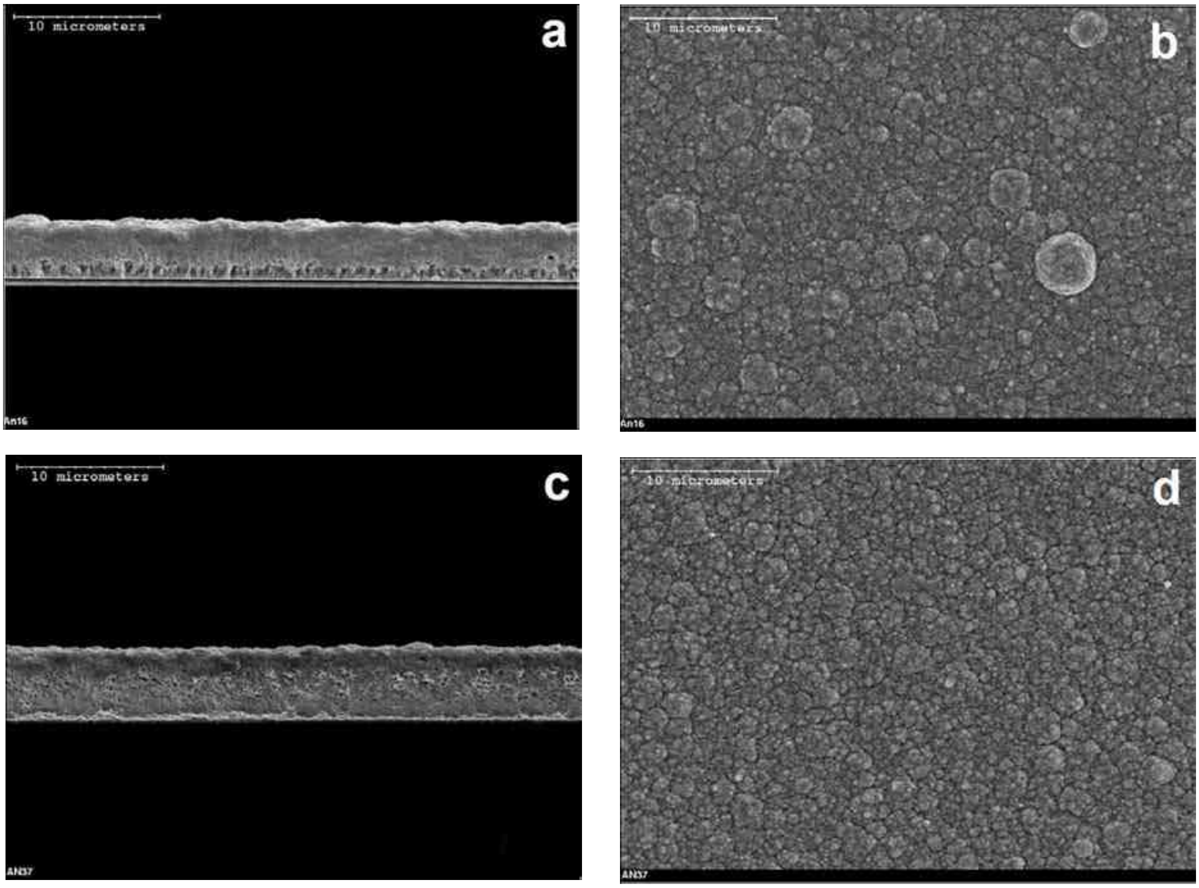

Figure 2—*SEM cross-section and plan view images showing Au-Ni films electrodeposited at a current density of 4.0 mA/cm^2 for 30 min: (a) and (b) Solution III; (c) and (d) Solution IV.*

evenly throughout the film, except for a few nanometers adjacent to the platinum seed layer. Here the gold is deposited preferentially and the nickel content is slightly lower than in the rest of the film.

Hardness measurements of plated films showed that the hardness is ~80 VHN for films plated from Solution III and ~150 VHN for films plated from Solution IV. The hardening effect is mainly attributed to the fine grain sizes of the films.[13,14] The pulse plating process in the present work has the advantage of producing finer grain deposits than the DC process. This is because the high current density during the on time produces a high nucleation rate, which also leads to low porosity.[15]

Electroplating of Au-Co alloys

The development process for electrodeposition of Au-Co films is similar to that described above for Au-Ni plating, so the procedure will not be given in detail. Instead, the results will be summarized. The required cobaltous ion concentrations for the Au-Co solutions were found to be in the 0.117M to 0.178M range for cobaltous sulfate. The pH value for the Au-Co plating solutions was ~6.5. The films exhibited good morphology if plated at current densities less than or equal to 4.0 mA/cm^2, as shown in Fig. 5. Films plated at a current density of 4.0 mA/cm^2 had a plating rate about 10 μm per hour with a composition of 0.8 to 1.6 at% Co. The film hardness values were in the range of 88 VHN to 130 VHN. SIMS depth profiling showed that the cobalt was distributed evenly throughout the layer thickness, without the solute-deficient region near the seed layer observed for the Au-Ni deposits (Fig. 6). The reason for the different behavior is not clear, as both Co^{+2} and Ni^{+2} have similar reduction potentials.

Stability of electroplating solutions

As mentioned in the Experimental section, the solutions for both Au-Ni and Au-Co plating were all transparent, although they were green and pink, respectively. Both solutions remained transparent without any color change when they were stored in sealed glass bottles for two to three months. In some instances, however, small dark precipitates formed in the Au-Ni solutions. Electrodeposition using aged Au-Ni solutions produced continuous deposits. However, the densities were lower if the deposits were obtained from solutions aged for more than two weeks (Figs. 7a and 7b). Deposits were further degraded if the solutions were aged for three months (Figs. 7c and 7d). Therefore, the useful lifetime of the Au-Ni plating solutions is likely no longer than two weeks. For the Au-Co solutions, deposits with good morphology are obtained at a current density of 4.0 mA/cm^2 from solutions aged up to three weeks. After three weeks, deposits plated at 4.0 mA/cm^2 degrade (Figs. 8a and 8b) relative to those obtained from fresh solutions (Fig. 5). Deposits plated at 3.0 mA/cm^2 from aged solutions (up to three months) are still comparable to those obtained from fresh solutions (Figs. 8c and 8d). It should be pointed out that the pure gold plating solution has a long useful lifetime (almost six months),[9] so that alloy plating solutions (Au-Ni or Au-Co) can be prepared from pre-prepared gold solutions as needed.

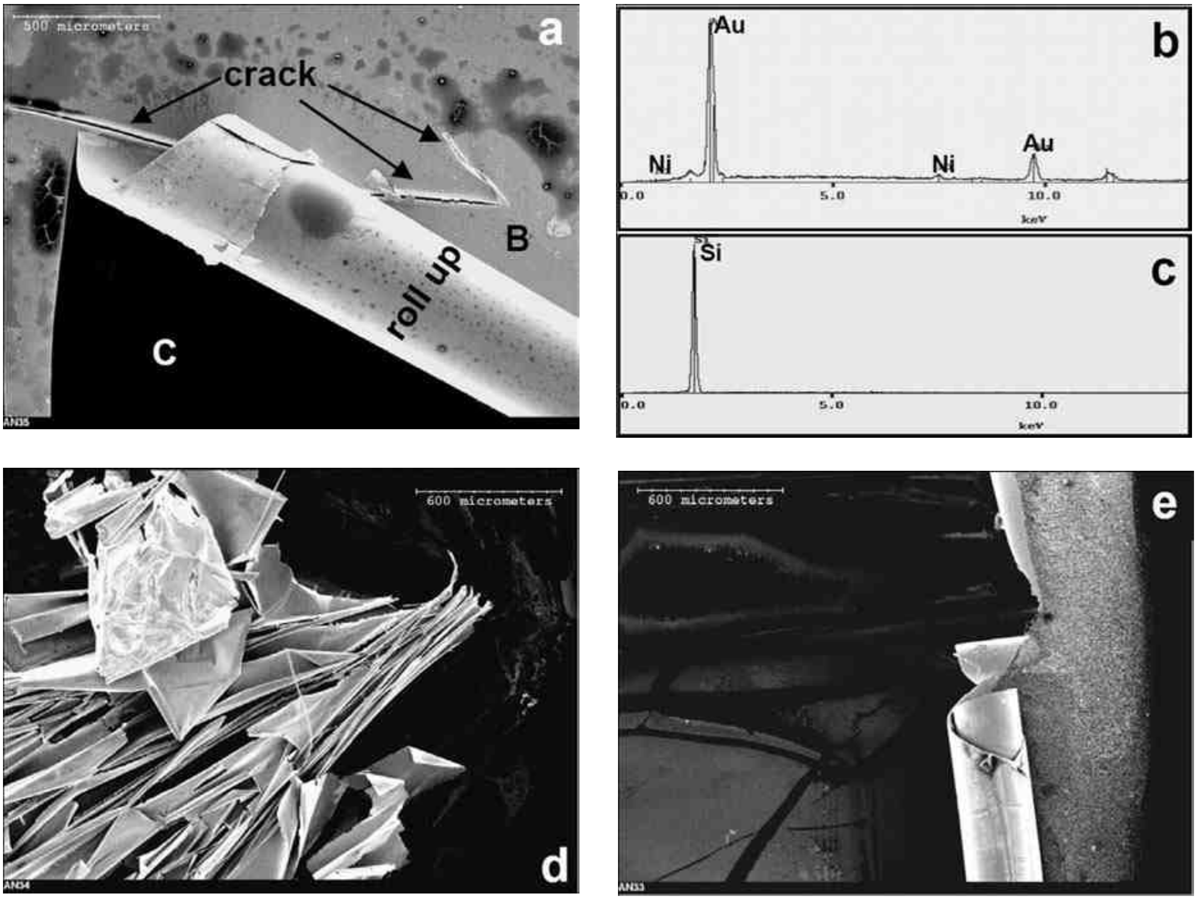

Figure 3—*SEM plan view images of Au-Ni films electrodeposited from Solution V for 30 min at current densities of (a) 2.0 mA/cm², (d) 3.0 mA/cm² and (e) 4.0 mA/cm². (b) and (c) are EDX spectra from position B and position C of (a).*

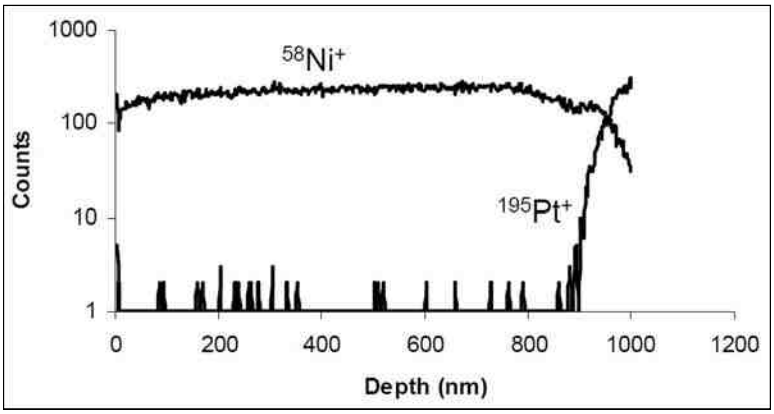

Figure 4—*SIMS depth profile for a Au-Ni film electrodeposited at 4.0 mA/cm² from a solution containing 0.140M nickelous chloride (Solution V). The platinum is the seed layer of the metallization.*

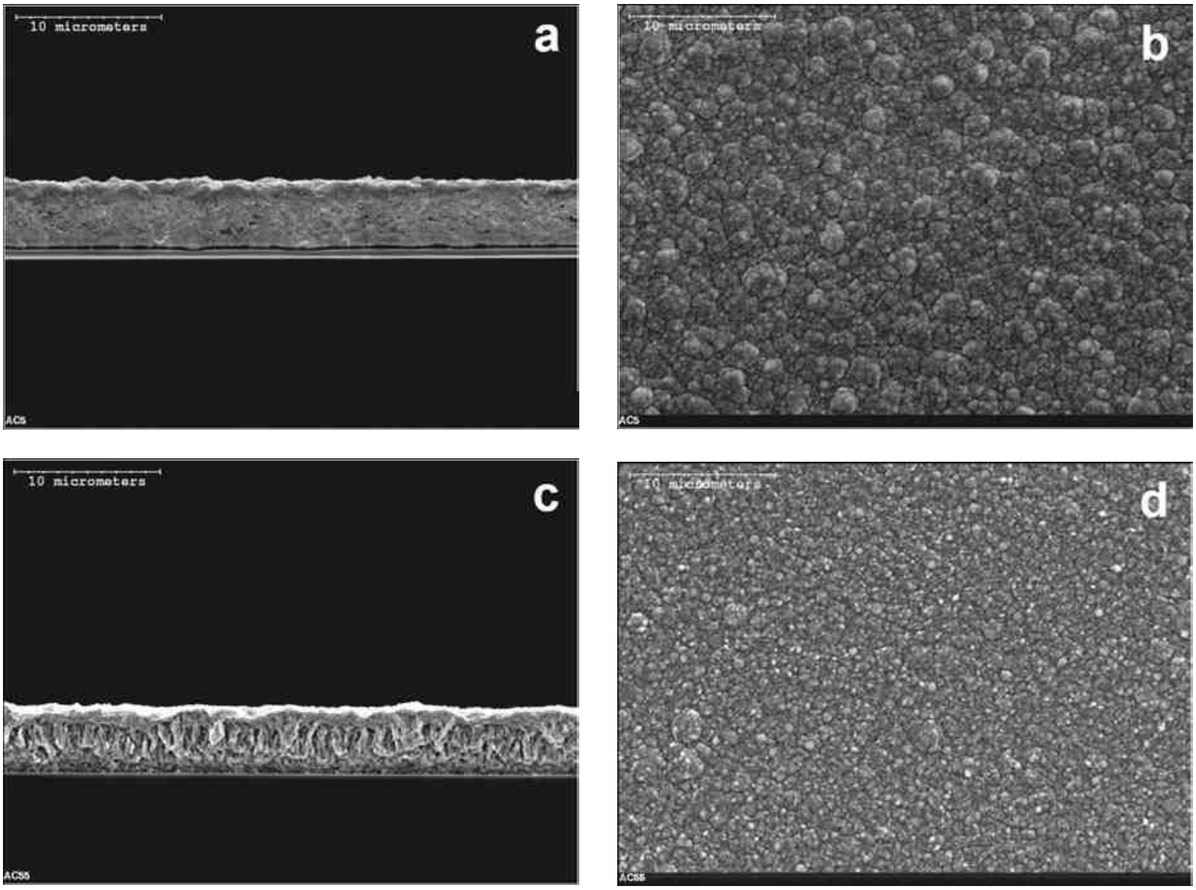

Figure 5—*SEM cross-section and plan view images showing Au-Co films electrodeposited at a current density of 4.0 mA/cm² for 30 min from solutions with cobalt concentrations of (a) 0.117M and (b) 0.178M.*

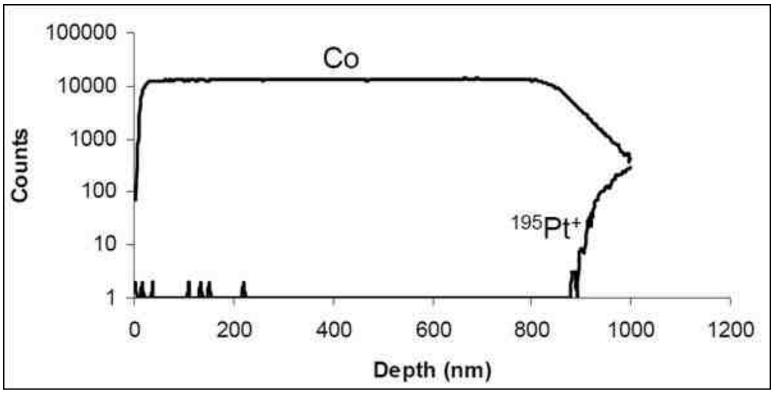

Figure 6—*SIMS depth profile from a Au-Co film electrodeposited at 4.0 mA/cm² from a solution containing 0.117M of cobaltous sulfate. The platinum is the seed layer of the metallization.*

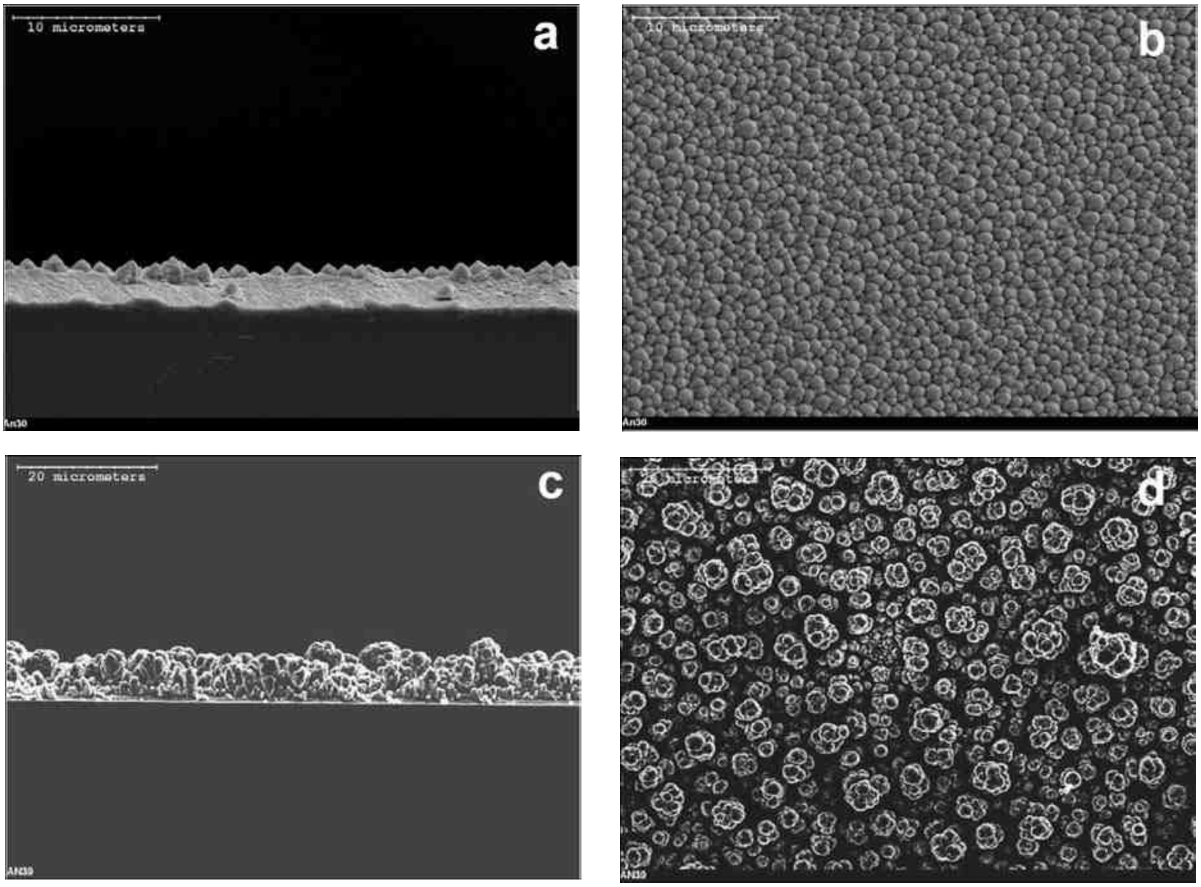

Figure 7—*SEM cross-section and plan view images showing Au-Ni films electrodeposited for 30 min at a current density of 4.0 mA/cm^2 from an Au-Ni plating solution (Solution III) aged (a) and (b) for two weeks; (c) and (d) for three months.*

Conclusions

Two hard gold plating baths without toxic components (such as cyanide or arsenic) have been developed based on a pure gold plating solution by the addition of nickelous chloride hexahydrate or cobaltous sulfate heptahydrate into the pure gold solution. The plating process can be carried out at room temperature. The electrodeposited films have hardness values of 80 to 150 VHN for the Au-Ni system and 88 to 130 VHN for the Au-Co system. The plating rate is about 10 μm per hour, for the concentrations examined, at a current density of 4.0 mA/cm^2. Stability testing shows that the useful lifetimes for the Au-Ni and Au-Co solutions are about two weeks and three weeks (at 3.0 mA/cm^2), respectively.

Acknowledgements

The authors would like to thank Dr. X. Tang of the Department of Chemical and Materials Engineering, University of Alberta for assisting in the film hardness measurements. The authors are also grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for providing research funding and Micralyne for providing metallized silicon wafers for electrodeposition. In addition, the Alberta Centre for Surface Engineering and Science (ACSES) is acknowledged for providing SIMS analysis.

References

1. I. R. Christie and B. P. Cameron, *Gold Bulletin*, **27** (1), 12 (1994); http://www.goldbulletin.org/assets/file/goldbulletin/downloads/Christie_1_27.pdf
2. Y. Okinaka and M. Hoshino, *Gold Bull*etin, **31** (1), 3 (1998); http://www.goldbulletin.org/assets/file/goldbulletin/downloads/Plating.pdf
3. P. A. Kohl, in *Modern Electroplating*, 4th Edition, M. Schlesinger and M. Paunovic, Eds., J. Wiley & Sons, NY, 2000; p. 207.
4. A.M. Sullivan & P.A. Kohl, *J. Electrochem. Soc.*, **144** (5), 1686 (1997).
5. J. Traut, J. Wright & J. Williams, *Plating & Surface Finishing*, **77** (9), 49 (1990).
6. *Gold Plating Technology*, F.H. Reid & W. Goldie, Eds., Electrochemical Publications, Ltd., Ayr, Scotland, UK, 1974.
7. W.S. Rapson & T. Groenewald, *Gold Usage*, Academic Press, Inc, New York, NY, 1978.
8. M. Guan & E.J. Podlaha, *J. Appl. Electrochem.*, **37** (5), 549 (2007).
9. A. He, Q. Liu & D.G. Ivey, *J. Materials Science: Materials in Electronics*, **20** (6), 543 (2009).
10. *ASM Handbook, Vol. 3: Alloy Phase Diagrams*, Hugh Baker, *et al.*, Eds., ASM International, Materials Park, OH, 1992; pp. 2-73.
11. M. Saitou, S. Oshiro & Y. Sagawa, *J. Applied Physics*, **104** (9), 093518 (2008).

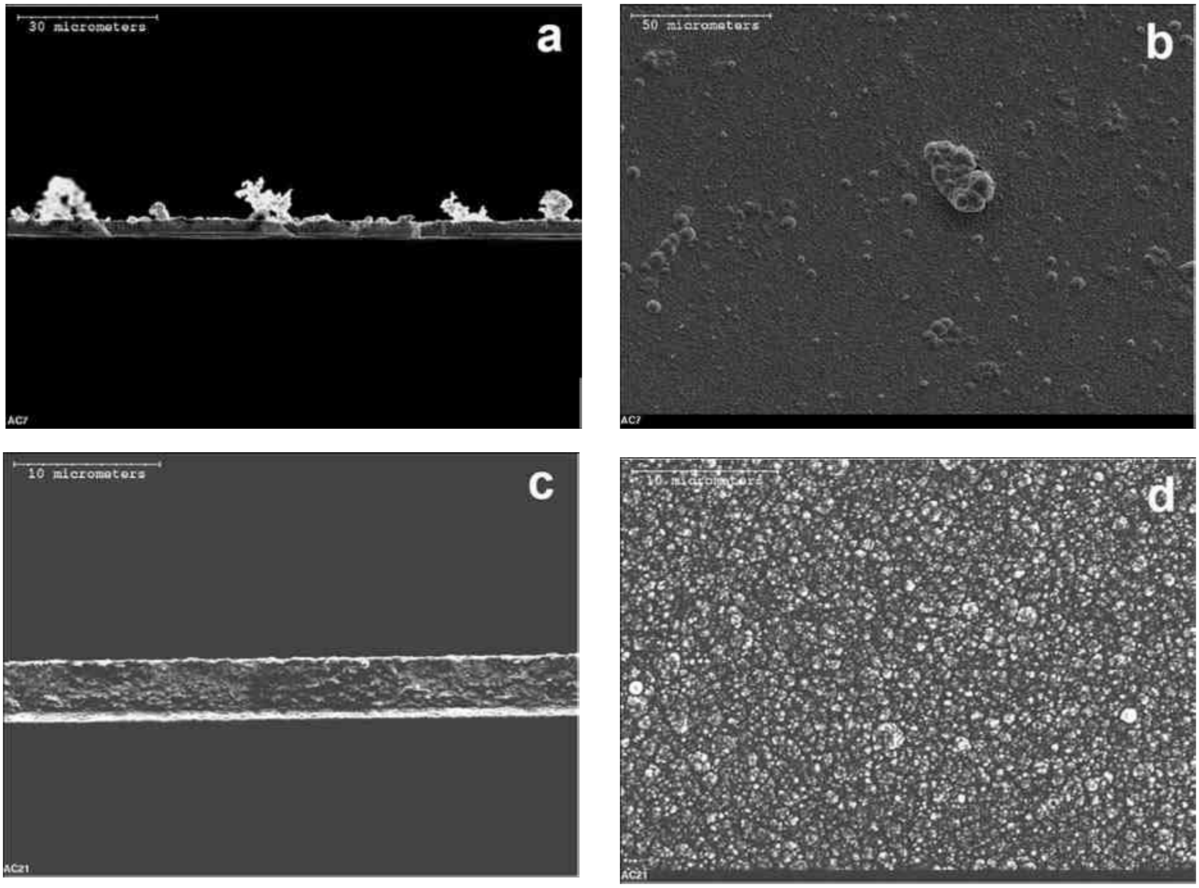

Figure 8—*SEM cross-section and plan view images showing Au-Co films electrodeposited for 30 min from an Au-Co plating solution aged (a) and (b) for three weeks (plated at 4.0 mA/cm^2); (c) and (d) for three months (plated at 3.0 mA/cm^2).*

12. M. Saitou, S. Oshiro & S.M. Asadul Hossain, *J. Appl. Electrochem.*, **38** (3), 309 (2008).
13. C.C. Lo, J.A. Aguis & M.R. Pinnel, *J. Applied Physics*, **50** (11), 6887 (1979).
14. F.B. Koch, *et al.*, *Plating*, **67** (6), 50 (1980).
15. G. Devaraj, S. Guruviah & S.K. Seshadri, *Materials Chemistry and Physics*, **25** (5), 439 (1990).

About the authors

Anqiang He

Qi Liu

Douglas G. Ivey

Dr. Anqiang He is currently a research associate in the Department of Chemical and Materials Engineering at the University of Alberta, Edmonton, Canada. He received his Ph.D. degree in materials physics from the Institute of Metal Research, Chinese Academy of Sciences in 1991. His research interests include materials science, surface science and electron microscopy.

Dr. Qi Liu obtained a Ph.D. from the University of British Columbia (Vancouver, Canada) in 1988 and is currently a Professor of Materials Engineering in the Department of Chemical and Materials Engineering at the University of Alberta. His field of study is solution and colloid chemistry in extractive metallurgy. Prior to joining the University of Alberta in 1998 he was actively engaged in materials engineering education, research and consulting at Wuhan University of Technology (China), The University of British Columbia and Process Research Associates Ltd (Vancouver, Canada).

Dr. Douglas G. Ivey is a Professor in the Department of Chemical and Materials Engineering at the University of Alberta, and director of the Alberta Centre for Surface Engineering and Science (ACSES). He received his Ph.D. in Engineering Materials from the University of Windsor (Canada) in 1985. His research focuses on applying high resolution microstructural characterization techniques to understanding the relationships between materials structure, properties and processing. Recent work has focused on developing "green" electrochemical techniques to deposit thin films and thicker coatings for a wide range of potential applications, from microelectronics to MEMS to fuel cells to supercapacitors.