IMAPS 2018 - 51st International Symposium on Microelectronics - Pasadena, CA USA - Oct. 8-11, 2018
Visit www.imapsource.org for more IMAPS papers

Reversed Pulse Plating of Silver-Cobalt for Connector Applications

Authors
Nazila Dadvand[a], Mina Dadvand[b], and Georges Kipouros[a]

Affiliations
[a]Dalhousie University, Mechanical Engineering Department, Halifax, Nova Scotia, Canada
[b]Institut National De La Recherche Scientifique (INRS), Varenne, Quebec, Canada

Abstract

The manuscript describes the use of anti-galling silver-cobalt alloy as a novel metallic contact finish for connector applications. The purpose of this work was to develop a cost-effective and cyanide-free and self-lubricated silver-cobalt alloy deposited using reversed pulse electrodeposition process for silver-based contact finishes in electrical contacts applications. The manuscript describes a novel silver-cobalt alloy deposited through reversed pulse-electroplating process that provides exceptionally low friction coefficient (similar to hard gold) and outstanding wear resistance compared to standard silver and any commercially available electroplated silver alloys such as silver-tin, silver palladium, silver antimony, silver-bismuth, silver-tellurium, and silver-tungsten.

Introduction

Most electronic connectors use electroplated hard gold as well as tin based alloys as contact finishes in order to protect the base metal of the contact from corrosive environment, and to optimize the properties of the contact surface in order to provide metal-to-metal contact [1,2]. The contact finishes provide protection against corrosion through sealing off the surface of the contact from environment [1,2]. However, the increase in the cost of gold metal has attracted interests in exploring of lower cost connector finishes [3]. Therefore, silver metal has been considered a potential alternative due to its interesting properties such as having somewhat noble nature compared to copper, excellent thermal and electrical conductivity, and lower cost compared to gold. However, there are issues associated with silver metal; for example, silver is much less noble compared to gold. Silver also has a poor wear resistance and high friction coefficient resulting in galling or adhesive wear [4-6].

The main focus of this research effort is to develop a suitable silver alloy with improved performance with regards to corrosion and wear resistance as well as friction coefficient compared to pure silver. The method of fabrication of such novel alloy should be economical and feasible for industrial applications. Therefore, a novel method based on reversed pulse electroplating process was developed to electroplate silver-cobalt alloy from an electroplating bath. Although there is little publication on electroplating Ag-Co; no report was found to demonstrate an electroplated Ag-Co with decent properties to be applicable in electronic industry [7-10]. Our newly formulated cyanide-free plating chemistry together with using a reversed pulse waveform with specific characteristics produced Ag-Co with outstanding properties that shows promising application in electronic industry.

Results and Discussion

Silver and cobalt have quite different potential reduction. Silver undergoes reduction much easier than cobalt [7-10]:

$$Co^{+2} + 2e^{-} \rightarrow Co \qquad E^{0} = -0.29 \text{ V vs. SCE} \qquad (1)$$

$$Ag^{+} + e^{-} \rightarrow Ag \qquad E^{0} = +0.80 \text{ V vs. SCE} \qquad (2)$$

Therefore, codeposition of silver and cobalt is very challenging. In order to decrease the difference in potential reduction of silver and cobalt, it is required to use an appropriate complexing agent(s) in plating solution. The complexing agent should have high complex formation stability with silver in order to reduce the potential reduction of silver. However, the decrease in potential reduction of silver decreases the deposition rate and efficiency. Our approach to overcome these limitations was to select a moderate silver complexing agent such as an amine based derivative of glycolic acid and apply an appropriate pulse reverse plating process to codeposit silver and cobalt without significant reduction in deposition rate. Figure 1 displays the reversed pulse waveform that was used for plating Ag-Co. As it can be seen, the pulse waveform is composed of two different cathodic currents (i_c (1) and i_c (2)), two different cathodic pulse duration (t_c (1) and t_c (2)), one anodic current (i_a), and one anodic pulse duration (t_a). The application of high cathodic current density (i_c (1)) for a short duration (t_c (1)) stimulates the nucleation of cobalt species. The high cathodic current pulse is then reversed. The reversed or anodic pulse has smaller current density with shorter pulse duration. The subsequent cathodic pulse current favors deposition of silver. The second cathodic pulse has smaller current density and longer duration compared to the first cathodic pulse (i_c (2) < i_c (1) and t_c (2) > t_c (1)).

It is possible that during the reversed pulse, some divalent cobalt ions (Co (II)) is oxidized to trivalent cobalt (Co(III)) followed by formation of hydroxylated cobalt. The formation of mixed $Co(OH)_2$ and $Co(OH)_3$ species at the cathode followed by immediate co-deposition with silver may be responsible for the observed greenish blue color the plated Ag-Co coating [11-12].

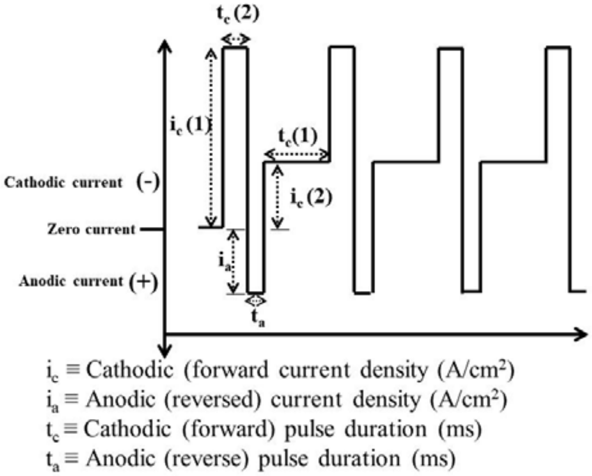

Figure 2. A schematic diagram of reversed pulse waveform for electrodeposition of Ag-Co coating.

Figure 3 displays the results of the reciprocating wear test for two different electroplated materials: standard pure silver deposited from a cyanide plating bath, and reversed pulse plated Ag-Co. Both standard silver and Ag-Co were deposited onto a nickel-plated copper substrate.

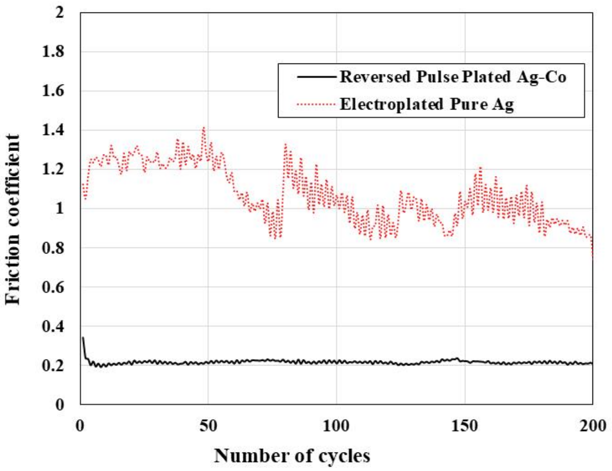

Figure 3. Coefficient of friction for 200 cycles of forward and backward wear passes comparing standard pure silver, and reversed pulse plated Ag-Co (containing 7 wt% Co). The applied load was 50 g. The test were performed at room temperature with 55% humidity.

As it can be seen, the reversed pulse plated Ag-Co demonstrated very low friction coefficient of about 0.2 (similar to hard gold) in comparison with the friction coefficient of standard pure silver. The standard silver was electroplated from a commercially available cyanide based plating bath.

Figure 4 shows SEM micrographs of the reversed pulse plated Ag-Co on nickel coated copper substrates before and after performing the reciprocal wear test. As it can be seen, the electrodeposited Ag-Co showed minimal wear track whereas the electrodeposited standard pure Ag displayed deeper and wider wear track after the test.

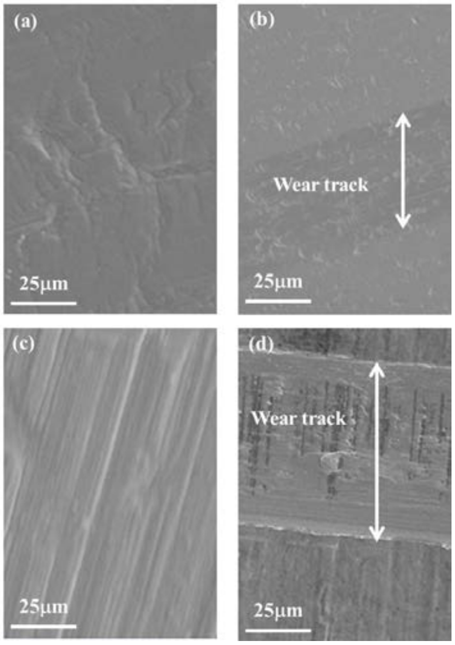

Figure 4. SEM micrographs of the electroplated of standard pure silver, and reversed pulse plated Ag-Co on nickel coated copper substrates before and after performing the reciprocal wear test. The applied load was 50 g load and the number of cycles was 100: (a) reversed pulse plated Ag-Co before wear test; (b) reversed pulse plated Ag-Co after wear test; (c) standard pure Ag before wear test; (d) standard pure Ag after wear test.

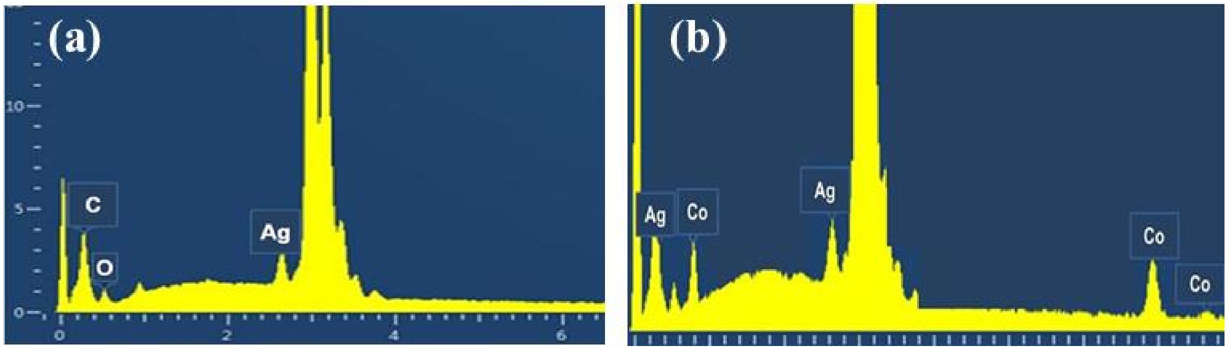

Figure 5: EDS micrographs for (a) standard silver and (b) reversed pulse plated Ag-Co.

Figure 5 shows EDS micrographs for standard silver and reversed pulse plated Ag-Co. The cobalt content of deposited Ag-Co was approximately 7 weight percent (wt%).

Conclusion

Reversed pulse electroplating process was used in order to electroplate Ag-Co coating on nickel-plated copper substrates. The use of an amine based derivative of glycolic acid as a compexing agent together with applying an appropriate reversed pulse plating waveform facilitated the codeposition of silver and cobalt despite of the large difference in potential reduction of silver and cobalt. The deposited material displayed low friction coefficient and high wear resistance compared to standard silver.

References

1. P. Slade, Electrical Contacts, Principles and Applications, New York: Marcel Dekker (1999).
2. G. Norberg, S. Dejanovic, and H. Hesselbom, Contact resistance of thin metal film contacts, Components and Packaging Technologies, IEEE Transactions on, 29 (2006) 371.
3. Y. Okinaka and M. Hoshino, Some recent topics in gold plating for electronics applications, Gold Bulletin, 31(1998) 3-13.
4. D. Jang and D. Kim, Tribological behavior of ultra-thin soft metallic deposits on hard substrates, Wear 196(1996) 171-180.
5. M. Myers; The Performance Implications of Silver as a Contact Finish in Traditionally Gold Finished Contact Applications, Proceedings of the fifty-fifth IEEE Holm Conference on Electrical Contacts (2009) 307-315.
6. M. Read, A. Weber, O. Yaglioglu, R. Martens, J. Lang, and A. Slocum, A two-coupon system or the repeatable measurement of flat on flat microscale contact resistance, International Conference on Electrical Contacts, Proceedings of, Jun. 2008.
7. S. Valizadeh, G. Holmbom, P. Leisner; Electrodeposition of cobalt–silver multilayers; Surface and Coatings Technology 105 (1998) 213–217.
8. E. Gomez, J. Garcia-Torres, E. Valles; Preparation of Co–Ag films by direct and pulse electrochemical methods; Journal of Electroanalytical Chemistry 615 (2008) 213–221.
9. N. Schuberta, M. Schneiderb, A. Michealis; The mechanism of anodic dissolution of cobalt in neutral and alkaline electrolyte at high current density; Electrochimica Acta 113 (2013) 748–754.
10. S. Nineva, T. Dobrovolska, I. Krastev, Electrodeposition of silver-cobalt coatings; Bulgarian Chemical Communications, 40 (2008) 248-253.
11. J. S. Santos, F. Trivinho-Strixino, E. C. Pereira; Investigation of $Co(OH)_2$ formation during cobalt electrodeposition using a chemometric procedure; Surface & Coatings Technology 205 (2010) 2585–2589.
12. W. J. Blaedel, and M. A. Evenson; Preparation of Cobalt(III) Complexes by Continuous Anodic Oxidation, Inorganic Chemistry 5 (1966) 944–946.