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Research Article
Effect of Pretreatment on Electroplating of Ni-Co Substrate Contaminated with Gold

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Abstract

Background: The Ni-Co alloy is one of the crucial substrate in electronic industries. However, the substrate is contaminated with gold which is transformed to gold oxide during heat treatment, thereby resulting poor coating on the substrate during electroplating and inefficient solderability. **Materials and Methods:** In this study, the effect of different substrate preparation parameters before electroplating was investigated. Apart from that, the steps of surface preparation were also modified. The study was conducted in the process line using actual methods of the electroplating process and the electroplating equipment/apparatus and the substrate being used in electronic industry. The materials used were contaminated Ni-Co substrate, which was electroplated with pure tin to form a coating on the substrate. Different types of acid was used as descale medium. **Results:** The investigation with modified electroplating parameter and modified existing descale parameter did not exhibit any significant improvement of the electroplated film adhesion. However, the modified precleaning steps exhibited significant improvement in adhesion of coating on the substrate surface and the rejection of substrate was completely eliminated. **Conclusion:** The variation of precleaning parameters using standard descale acid and electroplating parameters did not resolve the poor adhesion of electroplating film on the Ni-Co substrate. However, the modified precleaning steps with new descale acid provided appropriate coating of tin on substrate surface during electroplating. The non-adhesion issue was completely eliminated and efficient solderability was achieved. It was found that with standard substrate preparation steps but variation of electroplating parameters could not eliminate the defects formation. However, modified precleaning with new descale acid completely eliminated the non-adhesion problem. There were no defects even at the lower level of electroplating parameters. Thus, the material and power consumption during electroplating were reduced. Highly efficient solderability was achieved, thereby, eliminating the rejection of substrate to be used in electronic devices completely. Hence, it can be said that the reliability of the electronic devices was enhanced and the process became cost effective.

Key words: Electroplating, substrate preparation, peeling, descale, adhesion, solderability, concentration, current, contamination

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

There are numerous substrate materials which are used in electronic devices. One of the important substrate materials is Ni-Co alloys. The alloys have been widely used as an important engineering material in industry because of their high strength, good corrosion resistance, heat-conductive and electro-catalytic activity[1]. In the electroplating industry for semiconductors, the base material onto which the desired metal is plated is known as a substrate[2,3]. Here the substrate is a solid medium, which is coated by another substance by electrolysis is called electroplated[4].

Normally integrated circuits are composed of multi component electronic devices which are used in high tech applications like telecommunications, military equipment. They have also applications in medical devices for implant in humans to abort the attack of many life threatening illnesses[5,6]. The substrate material must be electroplated before using in integrated circuits. The plating should have specified thickness with no improper adhesion and adequate solderability[7]. It is of paramount importance to know why and how the electroplating should be done. One of the crucial electroplating materials is tin and it is used widely in the electronics industry due to their excellent solderability, electrical conductivity and corrosion resistance[8,9]. In addition to that, the tin plating also gives a low resistance to the friction surface between aluminum surfaces for internal combustion engine[10].

Precleaning is the prerequisite of electroplating process for proper adhesion of electroplating material on the substrate. Descaling is a process where an acid solution is used to clean the substrate. The process is known as electrolyte pickling[8]. The descale acid concentration, immersion time and descale current are crucial parameters for cleaning.

In this study, the effect of precleaning on Ni-Co substrate contaminated with gold is investigated. It was observed that by modifying the stage of precleaning, the substrate could be electroplated with tin without any defects and with excellent solderability, thereby, eliminating completely the rejection rate. As a result, cost related to rejection was removed completely and thus made the electroplating process cost effective.

MATERIALS AND METHODS

The substrate which was used for these experiments has gold coating on bottom surface and the top is contaminated with gold from spill over during the gold plating process. The substrate was subjected to heat treatment and as a result oxide is formed on the surface. The oxide is mainly composed of nickel, cobalt and gold which in turn prevent the adhering of tin on the substrate surface.

The substrate surface was processed in a standard industrial way, which is composing of electro degreasing and electro de-oxidation/deburring. The substrate was electroplated using tin electrolyte. Tin plating was chosen as a plating material due to its resistance to corrosion, tarnish and most importantly for it solderability[11]. A benchtop power supply with voltage and current regulator were used in this experiment. The substrate samples were taken from the same batch. The power is sourced from a rectifier which supplies adjustable voltage and current. The power source is usually sourced form a DC power supply which is regulated through a transformer or regulator[12].

The experiments were conducted under three different set conditions. In the first set, the electroplating process variables were changed, following the standard pretreatment steps. Three plating parameters: Plating acid concentration, the electrolyte concentration and the plating temperatures were considered. A design of experiment (DOE) was conducted using statistical tool to carry out the experiments. In Table 1 the experimental conditions are presented.

The second set of experiments was conducted using persulfate descaling for the pre-plating treatment. The parameters varied were the descale concentration, descale current and the immersion time of the substrate in descale. A DOE was carried out using the three variables and the experimental conditions are presented in Table 2.

In third set of experiment, sulfuric acid was used as descale followed by combination of sodium persulfate and hydrogen sulfate. This combination was a more aggressive type. The same variables were used like in second set of experiment and DOE was carried out. The experimental conditions are given in Table 3.

In Table 3 there are two different types of pre-cleaning which were carried out prior to plating. The first was the

Table 1: Experimental conditions for electroplating parameters under standard precleaning condition using DOE

	Factors		
Run condition	Concentration of tin in electrolyte (g L^{-1})	Immersion time (sec)	Current of plating (amp)
1	55	120	85
2	145	120	85
3	55	240	85
4	145	240	85
5	55	120	155
6	145	120	155
7	55	240	155
8	145	240	155
9	100	180	120

preclearing using sulfuric acid and the second was a combination of sodium persulfate and hydrogen sulfate. The substrate was soaked in natrium hydroxide bath before conducting the precleaning.

Table 2: Experimental conditions for precleaning using persulfate

	Factors		
Run condition	Concentration of descale acid (g L^{-1})	Immersion time (sec)	Descale current (amp)
1	55	55	1
2	55	35	1
3	55	35	24
4	55	55	24
5	100	45	12.5
6	100	45	12.5
7	100	45	12.5
8	145	55	1
9	145	35	1
10	145	35	24
11	145	55	24

The pre-cleaned substrate was characterized by EDX and SEM to check the presence of contamination. After electroplating, the adhesion of the plated film onto the substrate was tested by adhering a tape onto the substrate and removing it. The tape was visually inspected to check for signs of the plating film which peeled and adhered onto the tape. Following this solderability was carried out on all samples after electroplating using JEDEC standard using dip and look solderability method.

RESULTS AND DISCUSSION

Under all experimental conditions, the electroplated substrate was characterized before using in the integrated circuits of electronic devices. Visual inspection under microscope was done first to identify any notable defects. After visual inspection, the substrates were

Table 3: Experimental conditions for precleaning using combination of sulfuric acid with sodium persulfate and hydrogen sulfate

	Descaling with sulfuric acid			Descaling with sodium persulfate+hydrogen sulfate		
Run condition	Concentration (%)	Immersion time (sec)	Descale current (amp)	Concentration (g L^{-1})	Immersion time (sec)	Descale current (amp)
1	12.5	35	1	55	35	1
2	25	35	1	55	35	24
3	12.5	55	1	55	35	24
4	25	55	1	55	35	1
5	12.5	35	24	55	35	24
6	25	35	24	55	35	1
7	12.5	55	24	55	35	1
8	25	55	24	55	35	24
9	12.5	35	1	145	35	24
10	25	35	1	145	35	1
11	12.5	55	1	145	35	1
12	25	55	1	145	35	24
13	12.5	35	24	145	35	1
14	25	35	24	145	35	24
15	12.5	55	24	145	35	24
16	25	55	24	145	35	1
17	12.5	35	1	55	55	24
18	25	35	1	55	55	1
19	12.5	55	1	55	55	1
20	25	55	1	55	55	24
21	12.5	35	24	55	55	1
22	25	35	24	55	55	24
23	12.5	55	24	55	55	24
24	25	55	24	55	55	1
25	12.5	35	1	145	55	1
26	25	35	1	145	55	24
27	12.5	55	1	145	55	24
28	25	55	1	145	55	1
29	12.5	35	24	145	55	24
30	25	35	24	145	55	1
31	12.5	55	24	145	55	1
32	25	55	24	145	55	24
33	18.75	45	12.5	100	45	12.5
34	18.75	45	12.5	100	45	12.5
35	18.75	45	12.5	100	45	12.5

Table 4: Plating thickness (mils) under various electroplating conditions and exposed substrate base metal after peel test

Run	1	2	3	4	5	6	7	8	9
Thickness (mils)	40	42	41	40	65	85	85	85	85
Exposed base metal (%)	90	92	91	95	97	96	92	91	95

Table 5: Exposed substrate base metal after peel test when descaled with persulfate

Run	1	2	3	4	5	6	7	8	9	10	11
Exposed base metal (%)	35	34	39	38	29	31	39	31	32	27	28

characterized by Scanning Electron Microscope (SEM), Electronic Dispersive Scanning (EDX), peel test and solder test.

Substrate electroplated under standard precleaning condition: The variation of electroplating parameters under standard precleaning only affected the thickness. Table 4 shows that, the texture of thickness varied significantly with the variation of electroplating current and time.

The plating filament peels off from the substrate with improper adhesion after the peel test. The thickness of coating on the substrate was only varied with the change of the parameters. The exposed base metal was still present on more than 90% of the substrate surface as presented in Table 4. In Fig. 1, the improper adhesion on the substrate surface is shown. As a result the substrate was rejected for further processing. As explained by Clark the peeling of the plating is always caused by a contaminated or oxidized surface which in this case is the oxidized gold on the substrate as identified by EDX and SEM[13].

The EDX analysis as presented in Fig. 2 indicates the presence of gold oxide on the electroplated surface. The presence of contamination is further verified by SEM micrograph as presented in Fig. 3. A dark region is observed in SEM micrograph which is due to contamination of gold. The gold was oxidized during heat treatment and was not removed by standard precleaning causing poor adhesion and peeling of coating[14,15]. The observation is supported by NPCS Board of Consultants and Engineers which stated that oxidized surfaces are formed during heat treatment of substrate which is a requirement before precleaning[13].

The electroplated surface was tested for solderability and is presented in Fig. 4. Figure 4 indicates inefficient soldering and rejection of substrate for further processing. Due to improper adhesion, solderability was not effective and failed in solder test as per the JEDEC J STD 002A requirement which states that the wetting area has to be greater than 95% solder coverage for the parts to be accepted[9].

Hence, it can be said that the electroplating parameters do not have a major role in eliminating defects unless the substrate is properly prepared before plating. It was envisaged

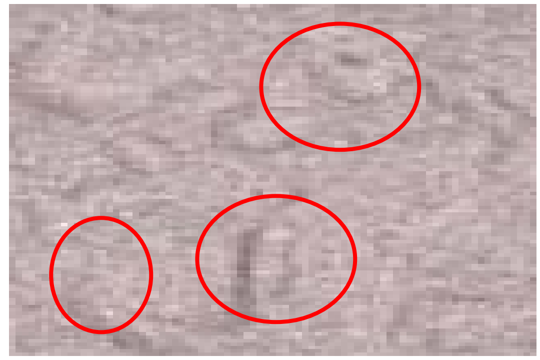

Fig. 1: Improper adhesion of plating onto substrate after standard precleaning

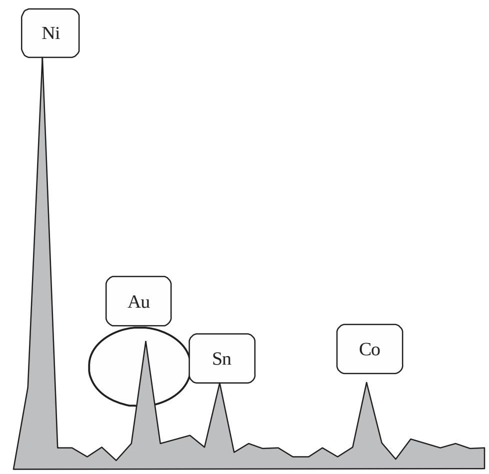

Fig. 2: EDX after precleaning under standard condition

that plating bath contaminated with metallic components could cause poor adhesion. Hence, experiment was conducted by making a new electroplating bath[13,16] but without any improvement. It was further explained by Clark that the plating bath does not play any role on the peeling of the plated surface from the substrate[14].

Substrate electroplated using persulfate as pretreatment acid: When the surface was pretreated with persulfate before electroplating, the pretreatment variables did not improve the improper adhesion effect significantly as given in Table 5. The improper adhesion is presented in Fig. 5 which shows the reduction of improper adhesion surface in comparison to Fig. 1. The EDX analysis, SEM photographs are presented in Fig. 6 and 7. Both the analysis shows the presence of foreign elements that is gold. The contamination caused improper adhesion[8] which ultimately resulted in effective solderability as delineated in Fig. 8.

Substrate electroplated using modified pretreatment process: The percentage of exposed substrate when pretreated with sulfuric acid combined with sodium persulfate and hydrogen sulfate and electroplated is given in Table 6. It is observed from the Table 6 that presence of improper adhesion on the substrate surface is less than 1% when lower level of acid concentration, immersion time and current is used for electroplating. With the upper and medium level of three variables the improper adhesion formation was prevented completely as given in Fig. 9. Hence, there was no failure in peel test. In Fig. 10-12 the EDX, SEM and soldering are presented.

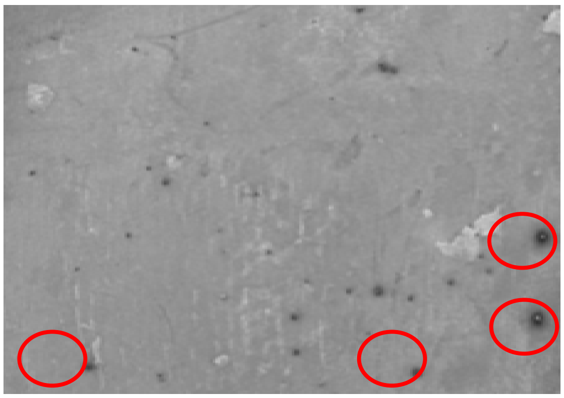

Fig. 3: SEM after standard precleaning of surface

Fig. 4: Solder test after electroplating with standard surface cleaning

The EDX analysis shows the absence of impurities in the form of oxide or foreign elements on the substrate. The absence of dark spots is also indicated from the SEM as shown in Fig. 11. The solder test under modified pretreatment also resulted effective soldering as presented in Fig. 12.

However, the other characteristics did not improve with the variation of electroplating parameters. This variation of the plating thickness was also observed by Wahab *et al.*[17] which showed a correlation between the electroplating time and coating thickness. This was further explained by Popoola and Fayomi[18] where the correlation of the immersion time with the coating thickness was shown. The results from this run

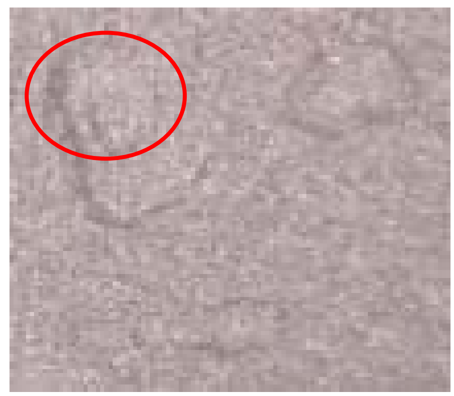

Fig. 5: Improper adhesion of plating onto substrate

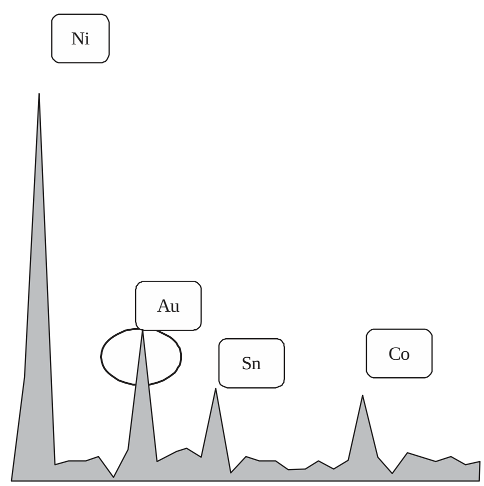

Fig. 6: EDX after descale with persulfate

Table 6: Exposed substrate base metal after peel test using modified pretreatment

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Exposed base metal (%)	0.19	0	0	0	0	0	0	0	0	0	0.37	0.13	0	0.78	0	0	0	0	0	0	0.53	0.62	0.38	0.22	0	0	0	0	0	0	0.85	0	0.08	0	0.19

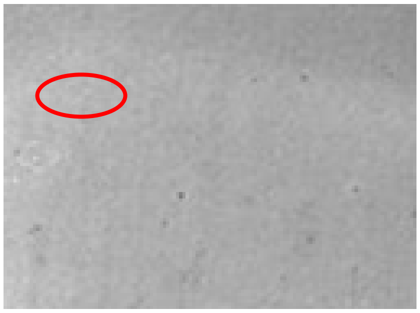

Fig. 7: SEM after descale with persulfate

Fig. 8: Solder test after electroplating with persulfate as descale

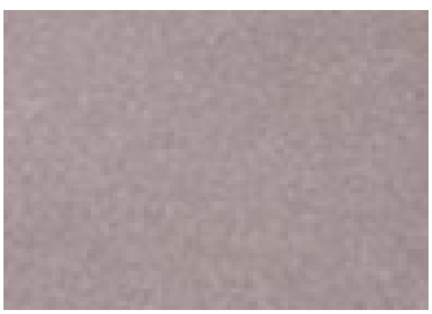

Fig. 9: Plating with good adhesion onto substrate under modified precleaning

showed that in addition to the electroplating time, the electroplating current was observed in the study to play a role in the thickness of the coating. In another study carried out by Popoola *et al*.[19] it showed that for the case of aluminum plating over a substrate, an increase in the plating film thickness causes an increased surface nuclei topography arrangement, strong surface adhesion and a smooth and shiny intermetallic coating formation, however, the study was not carried out on a substrate surface which was contaminated which has a severe effect on the adhesion of the plating film.

The study carried out by Salleh and Krishnan[20] showed that different types of descale had different effects on heat

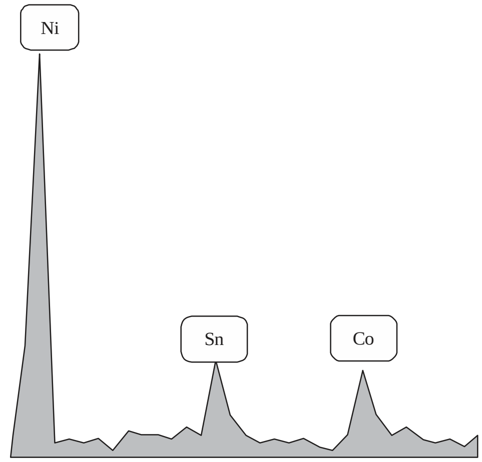

Fig. 10: EDX after descale with modified process

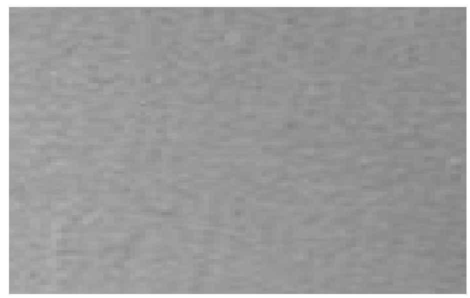

Fig. 11: SEM after descale in modified process

Fig. 12: Solder test after electroplating with modified precleaning

scale, oxide and contaminant removal from the substrate prior to plating. These heat scale and oxide removal played a part in the adhesion of the top plating film which indirectly contributes to good solderability. In addition to that Smaga *et al*.[21] also studied the adhesion properties and developed a surface preparation procedure to ensue good adhesion of the electroplating film over the substrate after electro plating through the proper removal of the oxide layer on the substrate. These results from these two studies using different types of substrates for electroplating addresses the

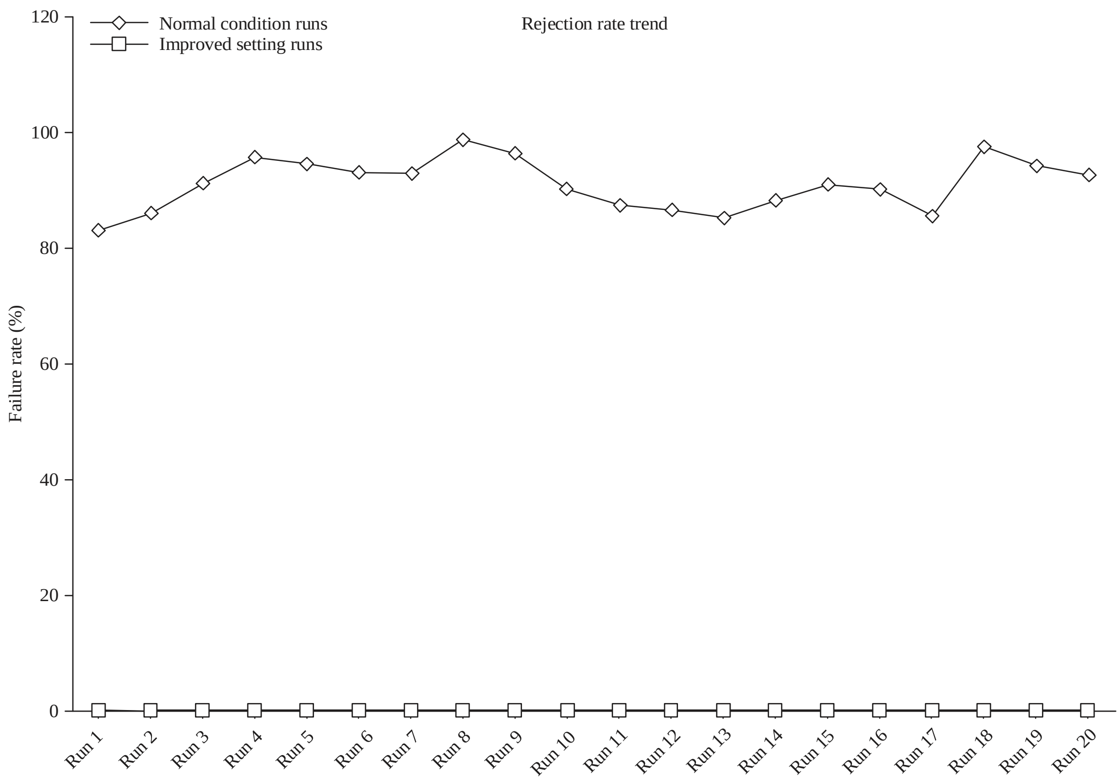

Fig. 13: Rejection rate trend for old vs new precleaning method

adhesion issue of the electroplating film which is similar to the study carried out for the nickel cobalt which was contaminated by oxide, where the oxide and contaminants on the substrate interfered with the adhesion of the tin electroplating film.

Hence, it can be said that the burrs or oxides are completely removed by modified pretreatment with sulfuric acid. The solder test under modified pretreatment also resulted effective soldering. By modified pre-treatment and combination of pre-cleaning chemicals could resolve the issue of contaminated oxide formation over the substrate during heat treatment[8,22,23]. The oxide was chemically removed from the substrate surface by using sulfuric acid, which transformed the metal oxide into metal sulfate[24].

Reject comparison: The DOE 3 which was the improvised condition and was repeated for 20 batch runs and the result was compared with the existing runs under normal conditions. A comparison of the rejection trend was made for the runs under normal condition and the improvised condition and is presented in Fig. 13. Figure 13 indicates the complete elimination of rejection trend.

CONCLUSION

The effect of pretreatment of Ni-Co surface before electroplating is promising. The variation of electroplating parameters with standard pretreatment could not improve the rejection rate of substrate to be used in integrated circuits for electronic industry. It only affects the appearance and thickness of the plating surface. Hence the electroplating conditions do not play any role in reducing the defect.

The formation of improper adhesion on the substrate and poor solderability is due to presence of foreign metallic elements on the substrate. By modifying pretreatment of substrate, it was possible to remove improper adhesion completely from the substrate, thereby, making efficient solderability without failure. The modification resulted complete elimination of rejection cost. The electronic industry will benefit from this excellent solderability.

SIGNIFICANCE STATEMENTS

- Usage of alloy metals as substrates in electronic manufacturing as the base of the integrated circuit chip

- Pre-treatment methods for nickel cobalt substrate prior to electroplating are studied
- Use of different descaling methods to prevent the plating film from peeling after the completion of the electroplating process
- Studies on the effect of different pre-cleaning and electroplating parameters on the adhesion of coatings are carried out
- Rejection of electroplated substrate was completely eliminated by applying modified pre-cleaning treatment before electroplating

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REFERENCES

1. You, Y.H., C.D. Gu, X.L. Wang and J.P. Tu, 2012. Electrodeposition of Ni-Co alloys from a deep eutectic solvent. Surf. Coatings Technol., 206: 3632-3638.
2. Lee, S.M., 1995. Dictionary of Composite Materials Technology. 1st Edn., CRC Press, Florida, ISBN: 9780877626008, pp: 138.
3. Bard, A.J., G. Inzelt and F. Scholz, 2012. Electrochemical Dictionary. 2nd Edn., Springer, New York, ISBN: 9783642295508, pp: 323.
4. Margaret Rouse, 2010. Part of the printers glossary: Substrate. http://whatis.techtarget.com/definition/substrate
5. Bauccio, M.L., 1993. Descaling and Special Surface: Treatments. In: Materials Properties Handbook: Titanium Alloys, Welsch, G., R. Boyer and E.W. Collings (Eds.). ASM International, Metals Park, OH., ISBN: 9780871704818, pp: 1145-1148.
6. Wang, Z., H. Jiang and H. Chen, 2014. Emerging Wireless Medical and Healthcare Applications. In: CMOS IC Design for Wireless Medical and Health Care, Wang, Z., H. Jiang and H. Chen (Eds.)., 1st Edn., Springer, New York, ISBN: 978-1-4614-9503-1, pp: 1-10.
7. Samuelson, J., H. Lawson and W.S. Dallas, 1863. The Popular Science Review 2. Robert Hardwicke, London, pp: 46.
8. Tan, A.C., 1993. Surface Preparation for Plating. In: Tin and Solder Plating in the Semiconductor Industry: A Technical Guide, Tan, A.C. (Ed.)., Cambridge University Press, London, pp: 90, 144-189.
9. Tong, X.C., 2009. Electrolytic Plating. In: Advanced Materials and Design for Electromagnetic Interference Shielding, Tong, X.C. (Ed.)., CRC Press, Florida, pp: 198-199.
10. Totten, G.E. and D.S. Mackenzie, 2003. Direct Tin Plating. In: Handbook of Aluminum: Volume 2, Alloy Production and Materials Manufacturing, Totten, G.E. and D.S. Mackenzie, (Eds.)., Marcel Dekker, New York, pp: 513.
11. Lowenheim, F.A., 1974. Tin Plating. In: Modern Electroplating, 3rd Edn., Lowenheim, F.A. (Ed.)., John Wiley and Sons, New York, pp: 377.
12. Pletcher, D. and F.C. Walsh, 1993. Electroplating. In: : Industrial Electrochemistry, 2nd Edn., Pletcher, D. and F.C. Walsh (Eds.)., Springer Science Macmilaina, Bangalore, pp: 368.
13. Durney, L.J., 1984. General Processing Data. In: Electroplating Engineering Handbook, 1st Edn., Durney, L.J. (Ed.)., Reinhold Publishing Company, New York, pp: 284.
14. Clark, R.H., 1985. Trouble Shooting. In: Handbook of Printed Circuit Manufacturing, 1st Edn., Clark, R.H. (Ed.)., Van Nostrand Reinhold Company, New York, pp: 361-363.
15. NPCS Board of Consultants and Engineers, 2003. Anodizing and Metal Treatment Hand Book. In: Alkaline Cleaning, NPCS Board of Consultants and Engineers (Ed.). 1st Edn., Asia Pacific Business Press, Delhi, pp: 63-65.
16. Bumiller, E.M., D.A. Douthit and J. Pecht, 2003. Contamination Source in Substrates. In: Contamination of Electronic Assemblies, 1st Edn., Bumiller, E.M., D.A. Douthit and J. Pecht (Eds.)., CRC Press, Florida, pp: 41-42.
17. Wahab, H.A., M.Y. Noordin, S. Izman and D. Kurniawan, 2013. Quantitative analysis of electroplated nickel coating on hard metal. Sci. World J., Vol. 2013. 10.1155/2013/631936
18. Popoola, A.P.I. and O.S.I. Fayomi, 2011. Effect of some process variables on zinc coated low carbon steel substrates. Sci. Res. Essays, 6: 4264-4272.
19. Popoola, A.P.I., O.S.I. Fayomi and O.M. Popoola, 2012. Electrochemical and mechanical properties of mild steel electroplated with Zn-Al. Int. J. Electrochem. Sci., 7: 4898-4917.
20. Salleh, R.B.M. and J. Krishnan, 2014. Copper descaling capability and material decision. Proceedings of the 36th International Electronics Manufacturing Technology Conference, November 11-13, 2014, Johor Bahru 10.1109/IEMT.2014.7123088.
21. Smaga, J.A., J. Sedlet, C. Conner, M.W. Liberatore, D.E. Walker, D.G. Wygmans and G.F. Vandegrift, 1997. Electroplating fission-recoil barriers onto LEU-metal foils for ^{99}Mo-Production targets. Proceedings of the 20th International Meeting on Reduced Enrichment for Research and Test Reactors, January 1997, Jackson Hole.

22. Crawson, R., 2006. Preplate Operations. In: Parts Fabrication: Principles and Process, 2nd Edn., Crawson, R. (Ed.)., CRC Press, Florida, pp: 293.
23. Stein, B., P. Jaeger and C. Przybyla, 2003. Mechanical Properties of Electroformed Nickel Cobalt Alloys. In: Heat Treating And Surface Engineering: Proceedings of the 22nd Heat Treating Society Conference and the 2nd International Surface Engineering Congress, Dahotre, N.B., R.J. Gaster, R.A. Hill and O.O. Popoola (Eds.)., ASM International, USA., pp: 308-319.
24. Wang, L.K., V. Eroglu and F. Erturk, 2009. Pickling Process Reactions and WPL Characteristics. In: Heavy Metals in the Environment, 1st Edn., Wang, L.K., J.P. Chen, Y.T. Hung and N.K. Shammas (Eds.)., CRC Press, Florida, pp: 295.