Bath and Deposit Monitoring System for Electroless Nickel Plating Process

ROBERT TENNO, KALLE KANTOLA
Department of Automation and Systems Engineering
Helsinki University of Technology
Otaniementie 17, 02015 TKK
FINLAND
http://www.control.tkk.fi

Abstract: - Electroless nickel plating is a widely used plating method in many industries. The usability of the coating is, however, restricted by the control problems related to the electroless nickel plating process. To ensure deposit quality, the transcendent properties of electroless nickel deposit should be accurately controlled during plating, which is challenging because of the spontaneous, unstable reaction and lack of online measurements. To improve operator based control, a special monitoring system for electroless nickel plating is presented in this paper. The monitoring system is calibrated especially to the electroless nickel process used for Plated-Through-Hole (PTH) board manufacturing. In the paper it is shown, that, the system is capable to estimate the electrical, chemical and deposit parameters of the plating process from standard measurements of nickel plating industry. The proposed monitoring system enables also the replace of the individual parameter supervision by the supervision of the overall process dynamics, i.e. the electrochemical processes.

Key-Words: - Monitoring, state estimation, electroless plating.

1 Introduction

Electroless nickel plating is one of the amorphous materials used in industry [1]. It is a widely used plating method in many industries, covering applications from oil and gas industry, machinery, etc. to electronic and micromechanic manufacturing [1]. The broad applications variety of the plating is because of the advances of electroless nickel coating, including uniform thickness distribution, high wear resistance and dense morphology [1,2]. These properties makes the electroless nickel alloy an excellent protection against oxidation and corrosion [3,4], which is its main use. If compared to electroplated nickel, the uniform thickness distribution of the electroless nickel alloy enables the plating of more detailed and challenging geometries [3].

In addition to these mechanical properties, the electroless nickel alloy is lead-free, which makes it a very usable for electronic applications, like in printed circuit boards (PCB), in which the lead is tried to be replaced by other materials. In electrical devices sold in the markets of European Union, the use of lead is even prohibited by legislation after 1.7. 2006 [5]. Therefore, it is likely, that the electroless nickel plating will be more popular in the future.

The usability of the coating is, however, restricted by the control problems related to the unstable and spontaneous electroless nickel plating process. These problems include, *inter alia*, the plating bath contamination [6], meaning the precipitation of the bath caused by the unbalanced and too aggressive reaction. In addition, the co-deposited phosphorous has a critical effect to the morphology and further to the properties of the deposit [1]. The control of the plating reaction is a challenging task, because of the lack of online measurements of the controlled parameters and because of the fact, that the exact reaction mechanism of the plating reaction is not known [1,7,8].

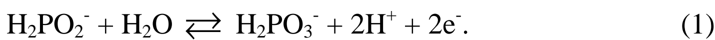
In this paper, a new model based monitoring system for the electroless nickel plating process is proposed. The monitoring system calibrated and tested especially to the electroless nickel process used for Plated-Through-Hole (PTH) board manufacturing, because the challenges of the electroless nickel plating are emphasized by the tight tolerances and challenging, detailed geometries of the PTH industry. The proposed monitoring system can, however, be applied also to other applications as well. The electroless nickel plating is an established process in manufacturing of printed circuit boards, where electroless nickel alloy works as a diffusion barrier between coppered circuitry and golden surface layer in so called electroless nickel immersion gold (ENIG) surface finish [1]. In this technology, the constricted spaces in conducting holes are plated with a thin nickel film containing predefined percentage of phosphorous ensuring a stress-free, dense morphology. Unfortunately, the most critical deposit parameters i.e. film thickness and phosphorous content cannot be measured online during plating. Instead, these parameters are measured indirectly after plating by X-ray fluorescence (XRF) based coating thickness gauge (CMI) analysis and wetting balance test with approximately 10 hours delay. Because of the long delay, these measurements are not suitable for effective process monitoring or control. Also, the possible errors in the deposit cannot be corrected afterwards and therefore, it is essential to monitor the plating reaction online during the plating to ensure a uniform quality of the deposit.

The proposed monitoring system provides essentially more information of the process online than the traditional methods provide offline. Besides the alloy thickness and phosphorous content, the system provides the bath parameters in terms of the electrical and chemical characteristics, which can be exploited to failure source detection and process control. The monitoring system is based on a model developed earlier by the authors [9,10]. This model has been validated before and therefore, not the model itself but only the monitoring system is analysed in this paper. The purpose of the paper is practical – to introduce an industrial application for the monitoring of electroless nickel plating process.

2 Reaction

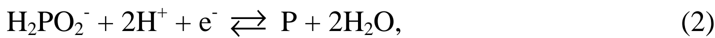
The hypophosphate reduced electroless nickel plating is a complex and challenging process. As a testimony of that, its reaction mechanism is not fully known but several mechanisms are proposed for the reactions [1,7,8]. At the moment, the electrochemical reaction mechanism is the most seconded one [1] and it is used by the authors as a base for the developed electroless nickel plating process model [9,10]. This model is applied for process monitoring in this paper. The model is based on the following anodic and cathodic reactions.

Anodic reaction – hypophosphite oxidation



$$H_2PO_2^- + H_2O \rightleftarrows H_2PO_3^- + 2H^+ + 2e^-. \quad (1)$$

Cathodic reactions – phosphorous deposition, hydrogen gas evolution, nickel deposition

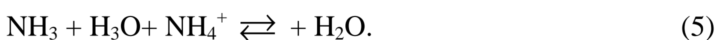


$$H_2PO_2^- + 2H^+ + e^- \rightleftarrows P + 2H_2O, \quad (2)$$

$$2H^+ + 2e^- \rightleftarrows H_2, \quad (3)$$

$$Ni^{2+} + 2e^- \rightleftarrows Ni. \quad (4)$$

In these reactions, the hydrogen ion production exceeds consumption and the degreasing of pH-index is balanced with ammonia additions, when the following neutralizing reaction takes a place



$$NH_3 + H_3O + NH_4^+ \rightleftarrows + H_2O. \quad (5)$$

In practice, the pH-index is increased depending on the metal turn over (MTO) to compensate the decreased reaction rates affected by the bath aging i.e. accumulation of the by-products like orthophosphate into the bath. Generally, the increased pH-index decreases deposit's phosphorous content degrading board's corrosion resistances [1,3]. Therefore a monitoring method is needed to determine the optimal plating conditions, related to the process state.

3 Model

The discharge model [9,10] of the reactions (1)-(4) is a two-directional electrode model where the current densities of the reactions are calculated from the Buttler-Volmer equation and controlled through empirical formulas accelerating or decelerating the reactions according to the concentration of reagents. The equilibrium potentials of the reactions (1)-(4) are calculated from the Nernst equation and a mixed potential from the current balance of the anodic and cathodic reactions. The concentration dynamics of the reagents is evaluated from the mass balance.

The model enables online estimation of the product parameters (film thickness, phosphorous weight percentage), along with the electrochemical parameters (deposition speed, mixed and equilibrium potentials, current densities) and the chemical parameters (reaction rates, hypo- and orthophosphate density, hydrogen evolution rate) from the measured pH-index, nickel concentration, reagent addition flow rates, bath temperature, plating time and bath loading. The data flow sheet is shown in Fig. 1. It represents a complex calculation engine (model calculation), which is not discussed in this paper but detailed description can be found from Tenno *et al.* [10].

This model-based monitoring provides the current state of the product (board) and bath parameters faster and more completely than in any laboratory analyses. In the case of a failure, it allows fast detection of the failure source, which is essential for failure correction. This monitoring system is discussed next.

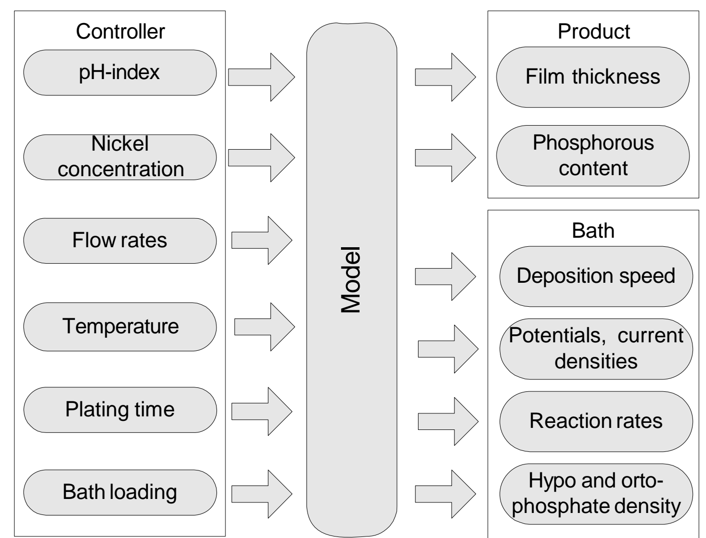


Fig. 1. Model-based process monitoring.

4 Monitoring System

The process monitor shown in Fig. 1 was integrated to the control system existing at a PTH factory. It is in interaction with the electroless nickel plating bath through the bath controller and flightbar controller as shown in Fig. 2. For time series analysis option, it is also in interaction with the laboratory database. Each element of the system has multiple functionalities described in the following.

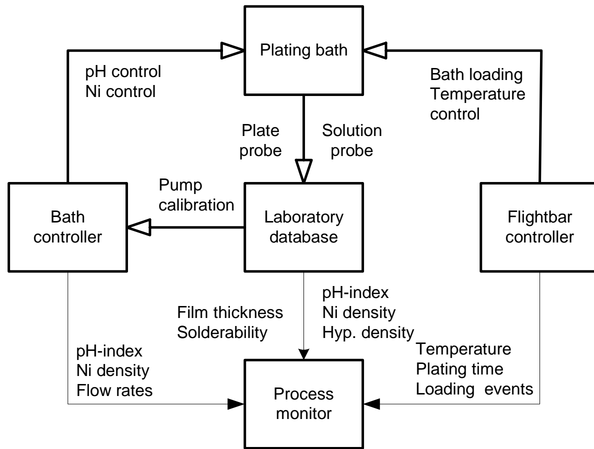


Fig. 2. The monitoring system in which the monitoring engine of Fig. 1 is integrated with the plating bath through the intermediate layer.

Bath controller This controller keeps the plating chemistry in balance by adding nickel sulphate, sodium hypophosphite and stabilisers in the bath. It also controls the pH-index according to the target profile.

Flightbar controller This is a transport crane, which immerses or elevates the PTH billets into/from the bath. It also manages the logging register and takes care of the plating temperature, performing measurements and heating.

Laboratory database The laboratory analyses carries out the final quality checking and supervises operators if some correction is required. The analyses include the product parameters (film thickness, wetting time and force), the bath parameters (pH-index, nickel and hypophosphite concentrations) and the calibration of the peristaltic pumps of the controller if some systematic deviation between online measurements and laboratory analysis is discovered.

Process monitor This computer characterises the current state of the process in terms of electrical, chemical and board parameters (see Fig. 1). It can also represent the plating history up to the current moment and compare these with the laboratory analysis. The process monitor downloads the latest data from the bath controller, flightbar controller and from the laboratory database.

Currently the monitoring system is under testing in the industrial plating process. One of the test runs is discussed next.

5 Monitoring Validation

The process monitoring system, shown in Fig. 2, is based on a process model which was originally calibrated on a large sample of industrial data and shown to be accurate [10]. Because of the model dependence, the monitoring systems accuracy is directly related to the accuracy of the process model. In this paper, the monitoring system is tested retrospectively on a large sample of independent industrial data shown below. This data represents the plating bath behavior during 6 bath lifetimes, which is equivalent to 284,390 PTH boards made. The monitoring validation is done by comparing the monitored values on the measured ones for the processes in which the measurements were available. This is done in Figs 3, 4, 5, where concentrations are compared to the laboratory analyses.

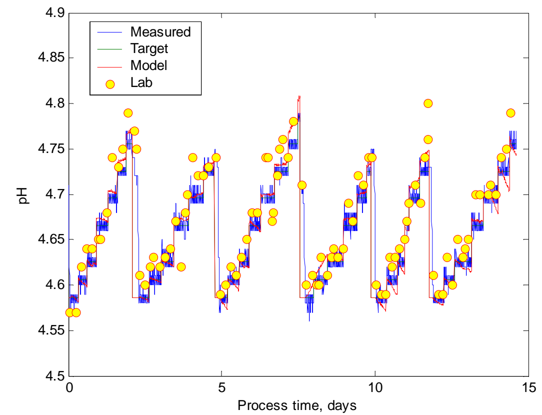


Fig. 3. The measured, model-predicted and laboratory-analysed pH-index.

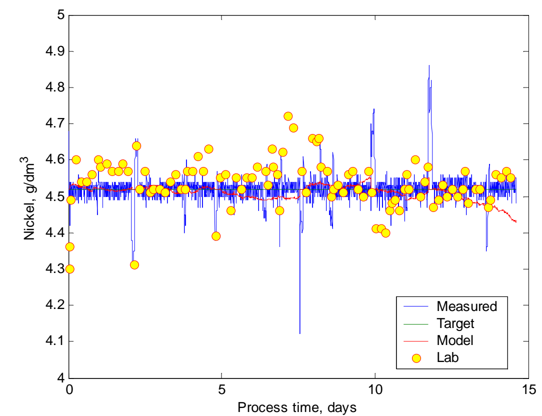


Fig. 4. The measured, model-predicted and laboratory-analysed nickel concnetration.

The monitoring model estimated and the measured pH-indexes are in relatively good agreement with each other and in moderate agreement with the results measured later in laboratory analysis as can be seen in Fig. 3. The same agreement is relevant to the nickel concentration shown in Fig. 4. However, there exists some error in nickel concentration estimate, which might be because of the error

in the flow measurements of the reagent additions. Despite this, the estimated nickel concentration seems to be closer to the laboratory measurements than the bath controller's ones. As discussed above, the bath controller adds nickel sulphate into bath to replace the nickel ions consumed by the reaction. The target is to keep the nickel concentration constant, which seems not be the case as can be seen from the figure, where the nickel concentration changes vigorously. These changes are because of the changes in the bath loading, which cannot be avoided in an industrial plating process. The proposed monitoring system might help to cancel the effect of the loading, because it takes the loading into account beforehand and therefore reacts more rapidly to the concentration changes that the analyzer of the bath controller.

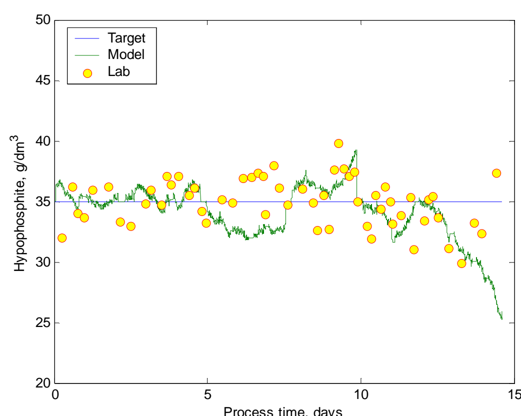


Fig. 5. The online-estimated hypophosphite concentration, compared to the results measured later in a labo-ratory.

The estimated and laboratory measures hypophosphate concentrations are presented in Fig. 5. As can be seen, the hypophosphate estimate follows the laboratory measurement and the estimation accuracy is related to the nickel estimation (Fig. 4). The hypophosphate works as a reducer in the studied process and its consumption is assumed to be related to nickel consumption. Therefore, its concentration is not measured by the bath controller, but the hypophosphate is added along with nickel addition. In a well balanced process, a hypophosphite concentration should be in balance with the nickel concentration, which seems to be the case if comparing the Figs. 4, 5. However, there exists some variation between the measurements. This variation is mainly because the fact that nickel takes a part only in reaction (4) while hypophosphate is involved in reactions (1) and (2). Therefore, the used control method is not accurate, but the hypophosphate should be controlled individually, which can be done by using the monitoring system. This would improve the bath balance and prevent the bath contamination affected by unbalanced bath [11].

In Fig. 6, the online estimated and CMI-measured film thickness (product parameter) is shown. The estimated and measured values seem to be relatively close to each

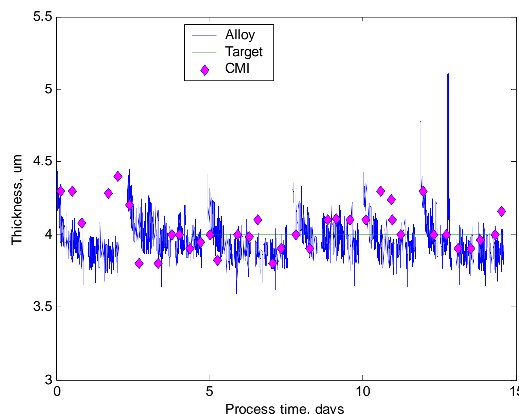


Fig. 6. The film thickness; estimated online and later measured in CMI analysis.

other and the trends of the measurements and estimation are the same. There are, however, some occasional exceptions, which might be caused by bath start ups or exceptional bath loadings. The peak values of thickness may be explained with the corresponding peaks of the measured nickel concentration (Fig. 4) and with the start-up concentrations of new baths (Figs 3, 7). The fast oscillation of the value is because of the corresponding changes in plating time and plating area. If the film thickness is compared with the measured pH-index (Fig. 3) or MTO (Fig 7), these seem to be related. This relationship is natural, because it is ob-served [1,2], that higher pH-index accelerates plating reaction while high MTO for its part decelerates plating rates. To guarantee stable product quality in PTH manufacturing, the plating rates are desired to keep constant and therefore, the decelerating affected by the MTO raise is compensated by increasing pH-index along with MTO. Currently, the target profile of pH-index seems to depend on the MTO-index as a linear function implemented through small steps as show in Fig. 3. This is not accurate enough and the target profile should be chosen more precisely if uniform quality is desired, as can be seen from the figure. This means that instead of linear stepwise relationship, the target profile should be continuously dependent on MTO and also reagent concentrations, like on nickel and hypophosphate concentrations.

In general, the phosphorous content depends on the pH and MTO-indexes [1]. In Fig. 6, the estimate of the phosphorous weight percentage, characterising the tensile strength and corrosion resistance of the film [1,7,8,12], is shown. As in the case of film thickness, the peak values of phosphorous may be explained with the corresponding peaks of the measured nickel concentration in Fig. 7 and somewhat less with the start-up values of a new bath (Figs 3, 7). The phosphorous content cannot be measured online and therefore no phosphorous measurement is presented as a validation reference. Phosphorous content is, however, closely related to solderability of PTH [13,14] and

therefore, it can be estimated from solderability measurements presented in the figure.

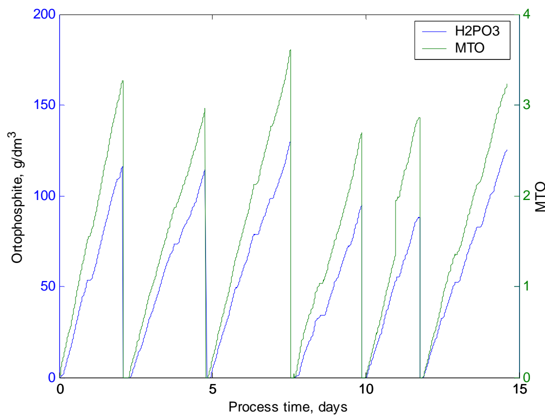


Fig. 7. The measured metal turn over and online-estimated orthophosphate concentration.

In solderability measurements the time T is the time when the solder reaches 2/3 of its maximum force and the wetting forces F1 and F2 are the maximum forces of the solder 2 and 4 second after soldering. Although, some correlation can be seen between the estimated phosphorous content and the solderability results (the phosphorous content correlates with the wetting time with a correlation coefficient = 0.14 and has almost no correlation (correlation coefficients -0.028, -0.023) with the wetting force), the estimation seems not be very accurate as can be seen from the figure. This might be, because of the solderability characteristics are affected not only by phosphorous content but also by many other factors like the cleanliness of the surface, activation of the surface, board aging at high temperature, nickel concentration in gold bath and gold layer thickness of ENIG surface. Therefore, it seemed that these characteristics alone are poor indicators for the phosphorus content of the film. The phosphorous content is, however, a critical parameter for corrosion resistance and therefore it should be supervised online. For that purpose, the proposed monitoring system seems to offer an effective tool.

6 Process Dynamic Analysis

Although, the reaction mechanism of the electroless nickel plating is not completely known, the complex relationships between the partial reactions of the process can be analyzed by using the online-estimates, provided by the monitoring system as discussed in the following.

In Fig. 8, the deposition speed of the deposit is decomposed to speeds of nickel and phosphorous depositions. While the total speed controls the film thickness (Fig. 6), the balance of its components controls the phosphorous content of the alloy (Fig. 9). This is because the deposited masses are integrals of the deposition speeds. The observed peak values in the deposition speeds are because of the corresponding peaks of the current densities (Fig. 10). The current densities are calculated from reagent concentrations through Buttler-Wolmer equation and the peaks in the current densities are, for their part, affected by the changes in reagent concentrations. The shapes of the deposition speeds and current densities curves are inherited from the equilibrium potential curves, shown in Fig. 11.

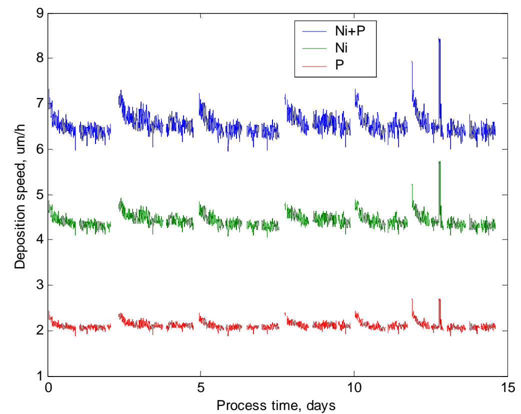


Fig. 8. The online-estimated deposition speed total for alloy and volumetric speed for nickel and phospho-rous.

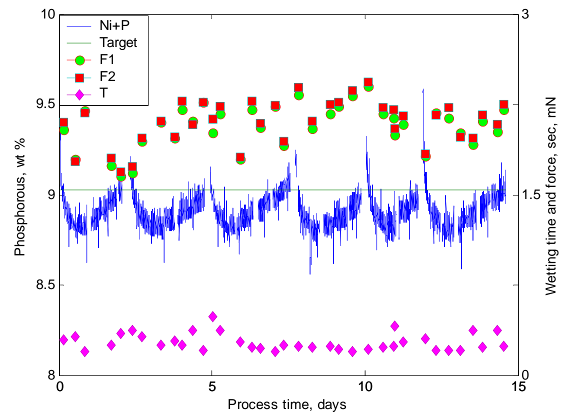


Fig. 9. The phosphorous weight percentage; estimated online and later measured wetting time (T) and forces (F1, F2).

The overpotentials i.e. the voltages between the mixed potential and equilibrium potentials (see Fig. 11), are inputs for the Buttler-Wolmer equation and, therefore, they control partly the current densities of the partial reactions (Fig. 9). Through Buttler-Wolmer equation, they affect on the deposition speed of nickel and phosphorous (Fig. 8) and eventually on the film thickness (Fig. 6) and phosphorous content (Fig. 9). Moreover, the over potentials and current densities are related also to the chemical reaction rates show in Fig. 12. The chemical reaction rates determine the concentration dynamics of the reagents and are also affected by the reagent concentrations itself. Therefore, direct relations between the overpotentials, current densities and

the reaction rates are rather hard to see by comparing the respective figures.

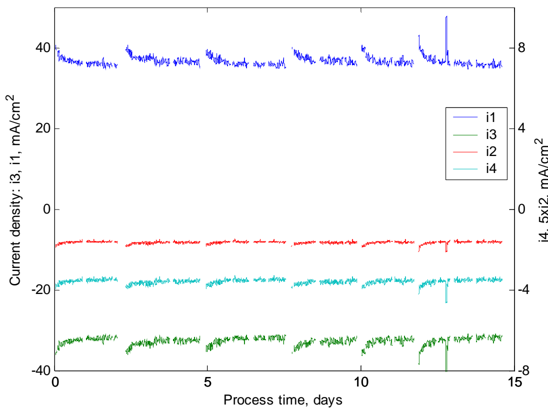


Fig. 10. The online-estimated current densities of hypophosphite oxidation (1), phosphorous deposition (2), hydrogen gas evolution (3) and nickel deposition (4) reactions.

In the reaction (3) hydrogen gas is formed from the hydrogen ions. An increase in gas formation is observed to precede the bath contamination by Winowling Jappes *et al.* [11] and therefore the estimate is important in process supervision. As can be assumed, the direct measurement of hydrogen gas evolution is difficult to carry out in an industrial process environment making the monitoring concept desirable. During the test, the hydrogen gas formation is rather unstable as shown in Fig. 13 where the graph is a half hour average. The formation rate is related to reaction rates which is natural: the hydrogen gas is a by product of the deposition reactions. In the case of unstable hydrogen evolution the phosphorous content between the film layers is hardly unique and a layered morphology or sometimes “black nickel” can be formed. The latter is closely related to weak solderability and is a problem in PTH technology [8].

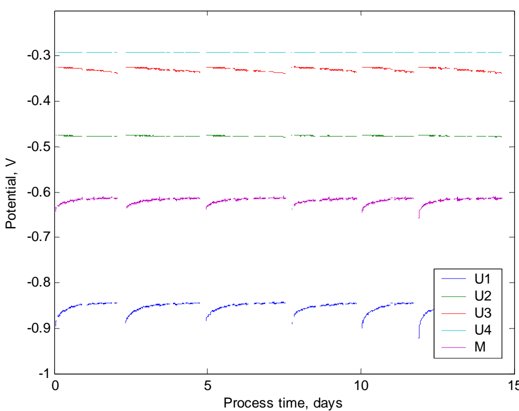


Fig. 11. The online-estimated mixed potential (M) and equilibrium potentials of hypophosphite oxidation (1), phosphorous deposition (2), hydrogen evolution (3), and nickel deposition (4) reactions.

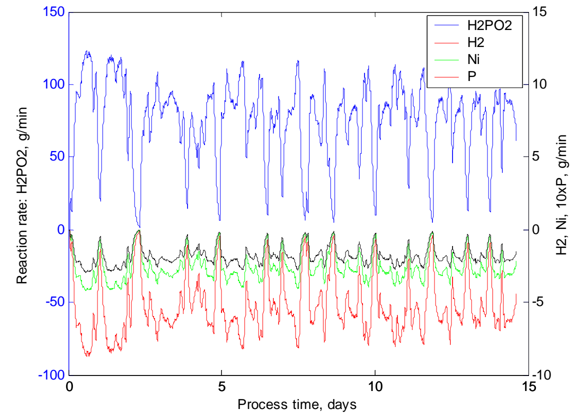


Fig. 12. The online-estimated reaction rates of hypophosphite oxidation (H2PO2), hydrogen gas evolution (H2), nickel (Ni) and phosphorous (P) deposition reactions.

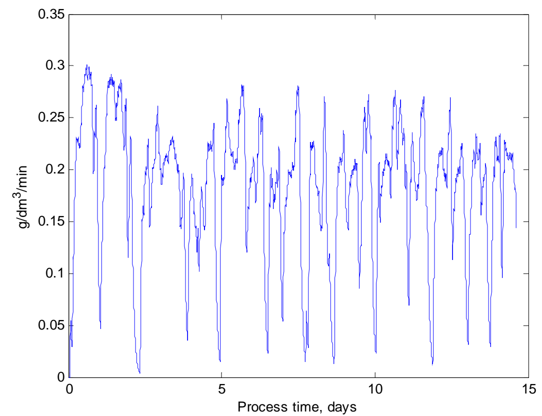


Fig. 13. The online-estimated hydrogen gas evolution.

As discussed, the concentration of species (pH-index, nickel, hypo- and orthophosphate) controls mainly the current densities, through Buttler-Wolmer equation, which furthermore controls reaction rates. Therefore, in electroless plating the concentrations are used for process control and especially the pH-index (Fig. 3) is used to compensate the reaction rate decrease caused by the bath aging. The bath aging characterised by the MTO-index is mostly due to the orthophosphate accumulation which might be a better indicator than MTO. Both of these are presented in Fig. 7. By comparing the figures 3 and 4, one can see that, on a contrary to pH-index, the nickel concentration is kept constant during plating. This control strategy is in disagreement with the stable thickness and phosphorous content requirement [6]. The phosphorous content estimate produced by the monitoring system can be used to control also the nickel concentration and thus cancel this disagreement.

As one can see from above, the electroless nickel plating reaction is a complex process in which several process parameters, like concentrations, temperature, loadings, bath aging, etc., affect greatly on the reaction through complex, rather contradictory manners. In the

process, a change in one parameter can easily eliminate the effect of several control efforts making the process monitoring and control difficult. In this kind of process, the supervision of some particular bath parameters does not guarantee a stable, uniform end product. Therefore, the supervision of some individual parameters should be replaced by the supervision of the overall process dynamics. In the case of electroless nickel plating process, this means that instead of supervision of individual parameter, like reagent concentrations, the electrochemical processes, like current densities and equilibrium potential, should be supervised. If the electrochemical core of the process is in balance, also the deposited alloy is uniform. Because the current densities cannot be controlled directly but, for example, through nickel concentration and pH-index, the individual process parameters is used for process control. In this case the correct control action can be decided by using process model implemented in the proposed monitoring concept.

7 Conclusion

In this paper a monitoring system for electroless nickel plating process was described. The system was tested with industrial data gathered from a PTH manufacturing line and it was shown that the complex process could be characterised online in terms of the electrical, chemical and product parameters, using a model-based monitoring system and standard measurements of the industry. Based on the industrial data, the monitoring system was used for reaction analysis of the electroless plating process.

The data provided online by the system is similar to the data acquired later from the laboratory analyses. In addition, it enables online state estimation of the process in terms of natural parameters and therefore provides an option for fast failure detection and correction which is essential in industrial processes.

The electroless nickel plating reaction is a complex process in which several process parameters affect greatly on the reaction through complex, rather contradictory manners. Therefore, it was proposed, that the supervision of some individual parameters should be replaced by the supervision of the overall process dynamics, i.e. the electrochemical processes. The process control is conducted by the control of the reagent concentrations in which the correct actions are decided by using the process model implemented in the proposed monitoring concept.

References:

[1] G.O. Mallory, The fundamental aspects of electroless nickel plating, Electroless plating: fundamentals and applications, ed. Mallory G.O. and Hajdu J.B. (Orlando: AESF Society 1990), pp. 1-56.

[2] G.G. Gawrilow, Chemical (electroless) nickel plating, (Redhill, United Kindom: Portcullis Press Ltd., 1979).

[3] R. Weil, J.H. Lee, I. Kim and K, Parker, Plating and surface Finishing, 62 (1989).

[4] Y.A. Huang, X.T. Zeng, X.F. Hu and F.M. Liu, Electrochemica Acta 49, 4313 (2004).

[5] European Parliament, Directive 2002/96/EC of WEEE, (2003).

[6] W.J. Cheong, B.L. Luan and D.W. Shoesmith, Applied Surface Science 229, 282 (2004).

[7] G. Salvago and P.L. Cavallotti, Plating 59, 665 (1972).

[8] Y.-S. Kim, H.-J. Sohn, J. Electrochem. Soc. 143 (2) 505 (1996).

[9] R. Tenno, K. Kantola and H. Koivo, Electroless nickel plating: PCB process modelling and estimation. Proc. AIChE Annual Meeting (Austin, Texas, AIChE 2004).

[10] R. Tenno, K. Kantola and A. Tenno, Electroless Nickel Plating Process Model for Plating Through Hole Board Manufacturing. J. Electron. Mater, Vol. 35, No. 10, 2006, pp. 1825-1836.

[11] J.T. Winowling Jappes, B. Ramamoorthy and P. Kesavan Nair, J. Mater. Process. Tech. 169 (2) 308 (2005).

[12] M. Goosey, Circuit World 28 (3) 36 (2002).

[13] N.M. Martyak and J.E. McCaskie, Plat. Surf. Finish 83 (22) 62 (1996).

[14] S.-W. Ricky-Lee, C.C. Yan, Z. Karim and X. Huang, Assessment on the Effects of Electroless Nickel Plating on the Reliability of Solder Ball Attachment to the Bond Pads of PBDA Substrate. Proc. IEEE Elec-tronic Components and Technology (Las Vegas, NV, USA 2000).