Title:

Selective electroless nickel deposition on copper as a final barrier/bonding layer material for microelectronics applications.

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Abstract:

A low cost, selective electroless metallisation of integrated circuit (IC) copper bond pads with nickel and gold is demonstrated. This metallurgy can function as a barrier layer/bondable material when deposited as a thin layer or as the chip bump for flip chip applications when deposited to greater heights. Four alternative activation steps for selective electroless nickel deposition on bond pad copper are demonstrated. Selective low cost deposition has been achieved with a proprietary electroless plating bath developed at NMRC and three commercial baths on both sputtered copper substrates and electrolessly deposited copper on titanium nitride barrier layer material.

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Keywords; Electroless deposition; Copper bond pads; Barrier layer; Flip chip

1. Introduction

Aluminium has been the metallisation of choice for interconnection on integrated circuits (ICs) and bond pads for the last 35 years. However, as the feature sizes on ICs are reduced to deep sub-micron dimensions some limiting problems with aluminium interconnections have become apparent. The principal limitations of aluminium tracks with very small cross-sections are firstly a high electrical resistance which leads to signal propagation delay and to increased resistive losses and heat dissipation and secondly an increased susceptibility to electromigration and early failure. Copper has emerged as the material to replace aluminium due to its inherently lower electrical resistance and lower susceptibility to electromigration. Accordingly, much work has

been carried out to develop IC level processing for copper deposition and patterning and the identification of suitable barrier layer materials to protect the active silicon from the deposited copper. Connection of the I/O pad of the IC to the substrate in the majority of cases is achieved using wirebonds. A process to enable wirebonds to copper bond pads involves the deposition of a further barrier layer and aluminium by conventional PVD techniques and use the standard wirebond processes developed for aluminium metallisation. A low cost alternative to this is the selective electroless nickel and immersion gold deposition of a barrier/bonding layer for wirebond applications [1] eliminating the requirements for expensive vacuum equipment, mask and etch processes. Flip chip attachment which is becoming more widespread particularly in advanced IC applications may also be facilitated by the electroless nickel/gold metallisation by increasing the deposit height.

2. Experimental.

The substrates for the electroless nickel deposition were sputtered copper (5000Å) on titanium (2000Å) on 1000Å thermally grown SiO_2 on 4" silicon wafers. The metals were deposited using a Nordiko DC Magnetron sputterer. The palladium activation solution used in this work consisted of a solution of 0.1g/litre of $PdCl_2$ acidified with 1 ml of concentrated (sp.gr. 1.18) HCl. The activation solution was used at a temperature of 20^{o}C. A 0.5M solution of dimethylamine borane was also used as a predip at 20^{o}C (pH = 9.33) to achieve selective electroless deposition. Electroless nickel baths were all hypophosphite-based operating at similar pH values of 4.6 to 5.0 at temperatures of 85 to 95^{o}C. The general characteristics of the baths investigated are listed in table 1. Immersion gold was deposited at a pH of 5.2 at 85 to 90^{o}C from a Schloetter Ormex Gold solution. Electroless copper was deposited from an Alfachimici formaldehyde-

based Cuprosure solution. The deposits were analysed by scanning electron microscopy (SEM) using a Hitachi S-4000 Field effect SEM with a PGT IMIX energy dispersive x-ray (EDX) system for elemental analysis. Deposit height and uniformity was also analysed with the aid of a Tencor Alpha-Step 200 surface profilometer. The adhesion of the electroless nickel deposit on sputtered copper was assessed by shear test analysis using a Royce Instruments universal bond test System 552. The wirebonding properties of the nickel/gold deposit were investigated with a Dage BT 22 bond tester. A 25 μm diameter Al/Si wire was bonded to plated pads and the bond assessed by pull-testing.

3. Results and Discussion.

The objective of this work was to selectively electrolessly metallise copper bond pads with barrier layer and/or bonding metals suitable for IC level Cu metallisation technology. To this end the plating process and the copper to barrier/bonding layer interface was to be studied. This work discusses the plating processes developed and secondly presents the analysis of the deposited metal including uniformity, adhesion, contact resistance and bondability.

Electroless deposition of nickel on copper using hypophosphite based chemistries is not autocatalytic and therefore the deposition of nickel requires an activation step to initiate metallisation. Plating processes were developed involving a copper clean, etch, activation and finally solvent rinse prior to plating. A proprietary electroless plating bath was developed at NMRC which exhibits a number of advantages over commercially available solutions in the bath make-up, such as the exclusion of mobile ions and a lower concentration of organic complexants. It also fulfils current and

expected health and environmental legislation and is compatible with organic based dielectric/patterning materials such as polyimide and photoresists. The NMRC nickel plating bath and three commercial plating solutions were used to electrolessly plate the patterned copper wafers. The general characteristics of the baths investigated are listed in table 1. The development of cost effective autocatalytic activation steps was investigated for the purpose of providing wider process applications than afforded by the established palladium activation step. The use of palladium nuclei as a seed to initiate metallisation has two distinct disadvantages i) it can lead to non-selective plating and ii) cost considerations. Three alternative activation processes were established and the influence of these and the palladium route on the electroless plating process and the nickel to copper interface was investigated.

3.1 Activation of copper substrates for electroless nickel deposition.

Palladium is commonly used in the PCB industry as an activator for electroless metal deposition. It may be employed to metallise non-conductors such as FR4 boards for printed circuits. Palladium nuclei in such processes are deposited as colloids with tin [2,3} non-selectively over the entire substrate. They act as nucleation sites for the subsequent metal deposition by catalysing the oxidation reaction. The controlled deposition of palladium nuclei to yield patterned substrates involves the optimisation of this process for the specific patterned substrates. Such control was achieved by manipulation of palladium activation solution concentration, operating temperature and substrate activation time. In this work selectivity was optimised by lowering the palladium activation solution operating temperature and minimising the substrate activation time both of which would lead to cost savings in a manufacturing process.

This work achieved palladium activation with the operating parameters of 2 seconds immersion at ambient temperature.

Alternative copper activation techniques, which did not incorporate palladium, were also investigated. The first involved the use a borane reducing agent (Dimethyl amine borane - DMAB). Copper is active for the oxidation of DMAB and therefore nickel from this bath may be deposited selectively on copper without additional activation. DMAB based baths are not as widely used as hypophosphite based baths due to their higher cost and slower deposition rate. In addition DMAB baths co-deposit lower concentrations of alloying elements depending on the pH of the solution{4,5} (<1% B for the solution used by comparison with 7-12% P from hypophosphite). It has been suggested that alloy deposits are better diffusion barriers by virtue of the localisation of the alloying element at the grain boundaries inhibiting diffusion paths [1]. A commercial nickel/boron plating solution, Shipley Niposit 468, was utilised to deposit a Ni/B seed layer upon which Ni/P alloy from the hypophosphite-based bath was autocatalytically deposited.

In the third activation sequence a concentrated solution of a borane reducing agent was used as a pre-dip prior to immersion in the Ni/P plating solution producing a selectively deposited Ni layer. The use of either a Ni/B plating solution or a borane solution provides a cost effective autocatalytic activation step and, in addition, precludes extraneous metals at the Cu/Ni interface.

The fourth activation type involved the activation of the acidic nickel solution by nickel-plating a catalytic sample prior to plating the copper substrates. The immersion of this active sample in the plating bath effected nickel deposition on the copper from a

hypophosphite-based bath without the direct contact between the active substrate and the copper substrate. Figure 1 displays the variation in deposit thickness with time observed when the four activation types were employed with the NMRC electroless nickel bath. Relatively low deposition rates have been obtained ranging from 3 μm/hr for borane activation to 8 μm/hr for palladium activation.

3.2 Deposition of Electroless nickel from commercial solutions.

Three commercial solutions were examined in this work as a comparison to the NMRC nickel plating bath. An Alfachimici Niflex SMT bath was chosen as the deposition rate quoted by the manufacturer (10-15 μm/hr) was intermediate between what had been achieved with the NMRC nickel bath (8 μm/hr) and that potentially achievable with two high deposition rate baths, Enthone Enplate Ni-865 and Canning (now MacDermid) Nimax SB (Table 1) The NMRC and commercial baths were based on similar bath chemistries at near-identical operating conditions, and would be expected to yield similar results. The commercial solutions gave higher deposition rates and were found to be less susceptible to the deactivation observed with the NMRC nickel plating bath. The most efficient solution was Enthone Enplate Ni-865 with a plating rate ranging from 8 μm/hr for borane activation to 26 μm/hr for palladium activation. The plating rate of the commercial acidic nickel solutions varied depending on the activation type employed as observed previously for the NMRC electroless nickel bath. Figure 2 displays the variation in deposition height with time observed when the four activation types preceded nickel deposition from the Enthone Enplate Ni-865 nickel bath. A summary of the deposition rates in μm/hr for all combinations of plating solutions and activation types is given in table 2.

3.3 Deposit uniformity.

The principle factors found to have an adverse affect on plating uniformity were bubble formation on the active sites during plating as a result of hydrogen evolution and the retention of these bubbles on the surface of the die. Good solution agitation and positioning of the sample to allow flow of solution across the die prevents the retention of bubbles at the sample surface and improves the plating uniformity. A plating holder was fabricated in teflon to permit solution access to all points of the 1 x 1 cm die used in the initial plating experiments. Application of these modifications afforded uniform nickel plating which meets the requirements of flip chip assembly. The SEM images in figure 3 display an array of 65 μm high nickel features plated in an Enthone Enplate Ni-865 bath for 3 hour which illustrates that uniformity is maintained over extended plating durations..

The bump height deposition uniformity over an extended 3 hour plating period was analysed using a Tencor Alpha-Step 200 surface profilometer. The results are given in table 3. The table indicates the excellent uniformity obtained with two of the commercial solutions when plated for 3 hours for the Enthone bath and 90 minutes for the Alfachimici bath. Selective, uniform, high deposition rate nickel presented in this work could be used as a chip bump material for flip chip interconnect as an alternative to the wirebond substrate of the low profile deposits. The results indicate that there is no significant advantage of one activation type over another with regard to nickel deposit uniformity for either of these baths. Various nickel plated feature shapes and sizes were also inspected to ensure uniformity was not pad size dependent. Figures 4 (a) and (b) illustrate a SEM image and corresponding surface profile of a patterned

copper wafer, activated using borane solution and plated in Alfachimici Niflex SMT for 1 hour. It can be seen for different feature shapes and dimensions that the nickel deposition is uniform.

3.4 Adhesion analysis.

A Royce System 552 universal bond tester was used to analyse the adhesion of the NMRC electroless nickel deposit on the sputtered copper substrate. Palladium activation was used to initiate electroless nickel deposition on the copper substrates. The average shear test values for 26 μm high deposits on 100 x 100 μm copper pads was 427g per pad with standard deviation of 47g. The tests indicate that the nickel to copper interface forms a strong bond with an average shear strength in excess of 400 g per pad.. The shear values obtained are sufficient for assembly using electroless nickel deposited by this process as the under bump metallurgy (UBM) or chip bump material.

3.5 Bonding properties.

The bonding properties of nickel/gold barrier layers were analysed by wire bonding 25 μm Al/Si wire to plated pads and the strength of the bond assessed by pull-testing using a Dage BT 22 bond tester. Copper wafers were a) palladium activated and b) borane solution activated and subsequently nickel-plated using the NMRC nickel bath to generate two sets of samples with nickel deposit thickness ranging from 1.4 to 6.7 μm. It was established that the bonding properties of electroless nickel deposits were independent of the activation type employed over the range of thickness tested. Table 4 displays the strengths required to pull 25 μm Al/Si wire from electroless nickel bond layers which were deposited on sputtered copper wafers using palladium activation

steps. The data in the table includes i) bonding both ends of the wire to the freshly cleaned copper substrate, ii) bonding between the copper substrate and the Ni/Au bond pad and iii) bonding both ends of the wire to adjacent Ni/Au plated pads. For both activation types, the bonding directly to cleaned copper gives a slightly stronger bond. However, the data indicates that a thin electroless nickel barrier layer is sufficient to provide a bonding surface for wirebond applications on the IC I/O pad.

Copper metallisation for integration in ULSI technologies deposited electrolessly has been investigated [7,8] as a low cost alternative to the electrolytic copper route. An electroless copper deposit was investigated in this work as an alternative to the sputtered copper substrate discussed earlier. The deposition process for electroless copper using the commercial plating solution, Alfachimici Cuprosure, on sputtered TiN wafers required an organic solvent and water rinse, an etch and activation sequence prior to plating. Samples plated for 10 minutes were approximately 0.2 μm thick and passed the tape pull test. When the plating time was extended to 30 minutes, the copper deposit thickness ranged from 0.8 to 1.2 μm and the deposit failed the tape pull test. However after annealing the sample at 350°C for 30 minutes in an oxygen-free environment the deposit passed the adhesion test. Furthermore, extending the plating time from 10 to 30 minutes decreased the metal deposition uniformity as illustrated in figure 5 for this commercial solution which is manufactured for thin film deposition. The deposition uniformity was measured using a Tencor Alpha-Step 200 Profilometer.

Three TiN samples with electroless copper deposits from an Alfachimici Cuprosure commercial solution at room temperature were prepared for adhesion analysis, table 5.

Samples 1 and 2 passed the tape test while sample 3 passed the tape test after heat treating the sample for 1 hour at 350 °C in an oxygen-free environment. Subsequently the three samples were nickel and gold plated using the commercial solutions Enthone Enplate Ni-865 and Schloetter Ormex Immersion Gold to produce a 5 μm nickel bonding layer and a 0.1 μm gold capping layer. The bonding properties of the Cu/Ni/Au finish were assessed by wire bonding 25 μm Al/Si wire to plated die. The evaluation criteria includes 1) bondable finish, 2) wire-bond pull strength. samples 1 – 3 were established to be bondable, with maximum reliability achieved for sample 1, table 5. The reliability of bonding was calculated on the basis of the number of missed bonds per 20 bonds attempted. The Cu/Ni/Au finish of sample 3 was not bondable. When attempting to wirebond to sample 3, it was noted that as the wedge tool came in contact with the Cu/Ni/Au finish, the metal layers collapsed in a manner which would suggest that a gas or vacuum existed within the layer. Such an observation may be explained by the mechanism of electroless copper deposition. The chemical process of electroless copper deposition is governed by the simultaneous reduction of copper and hydrogen,

$$Cu^{+2} + 2HCHO + 4OH^{-} \rightarrow Cu + 2HCOO^{-} + 2H_2O + H_2 (\uparrow)$$

Therefore, the probability of incorporating atomic and/or molecular hydrogen into the deposit is high, making electroless copper liable to high porosity and low ductility [**6**]. The entrapment of hydrogen gas during copper deposition and subsequent expulsion of the gas during heat treatment may create voids within the deposit which collapse when punctured during the wire bonding process.

Table 5 also lists the wire pull strengths required to break the aluminium wire bonds to the copper/nickel/gold finish of samples 1 and 2. The aluminium wire bonding strength in both cases exceeded the minimum pull strength required by MIL-STD-883E (1.5 gm for 25 μm Al/Si wire). An inspection of the bonding sites after pull testing revealed that the bond failures occurred on the aluminium wire at the heel (figure 6) and not at the copper/nickel/gold to aluminium wire bond site (the footprint).

4. Conclusions.

This work has demonstrated the low cost electroless metallisation of IC level copper I/O pads with nickel and gold which can function as a barrier layer/bondable material when deposited as a thin layer or as the chip bump for flip chip applications when deposited to greater heights. Four alternative selective activation processes have been identified for electroless nickel barrier layer deposition on copper. The process was developed for selective electroless nickel deposition at a high rate (25 μm/hr) using commercial electroless nickel plating solutions. Deposit uniformities of less than 2% within die were achieved. Electroless copper metallisation may be the final metallisation in future copper based IC technology and this work demonstrates of the compatibility of the current electroless nickel barrier layer with that metallisation. The deposited nickel layer was shown to be well adhered to the IC copper and the bondability of the deposit was shown to exceed international wirebond military standards.

Acknowledgements

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Table 1. Operating conditions and characteristics of the electroless nickel baths investigated.

Figure 1. Variation of deposit height with time for four alternative activation processes using NMRC electroless nickel bath. Activations were (o) Niposit 468 Ni/B, (x) Pd activation, (σ) Borane activation and (□) Solution activation.

Figure 2. Variation of deposit height with time for four alternative activation processes using Enthone Enplate Ni 865 electroless nickel bath. Activations were (O) Niposit 468 Ni/B, (6) Pd activation, (σ) Borane activation and (□) Solution activation.

Figure 3. SEM image of patterned copper wafer plated in Enthone Enplate Ni-865 for 1 hour.

Table 2 Plating rates (μm/hr) achieved with electroless nickel baths and four alternative substrate activation types.

Table 3 Nickel deposit height (μm) and standard deviation for two commercial solutions and three activation types.

Figure 4. (a) SEM image and (b) surface profile of a nickel plated patterned copper wafer, activated using borane solution.

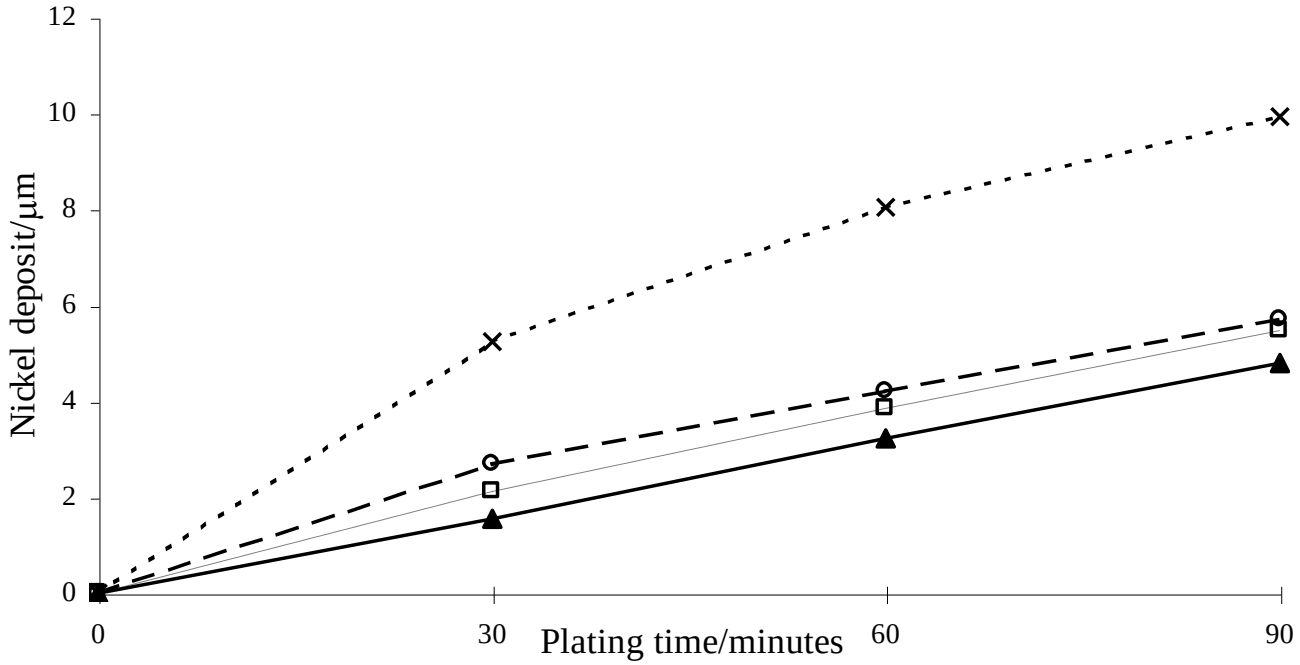

Figure 1

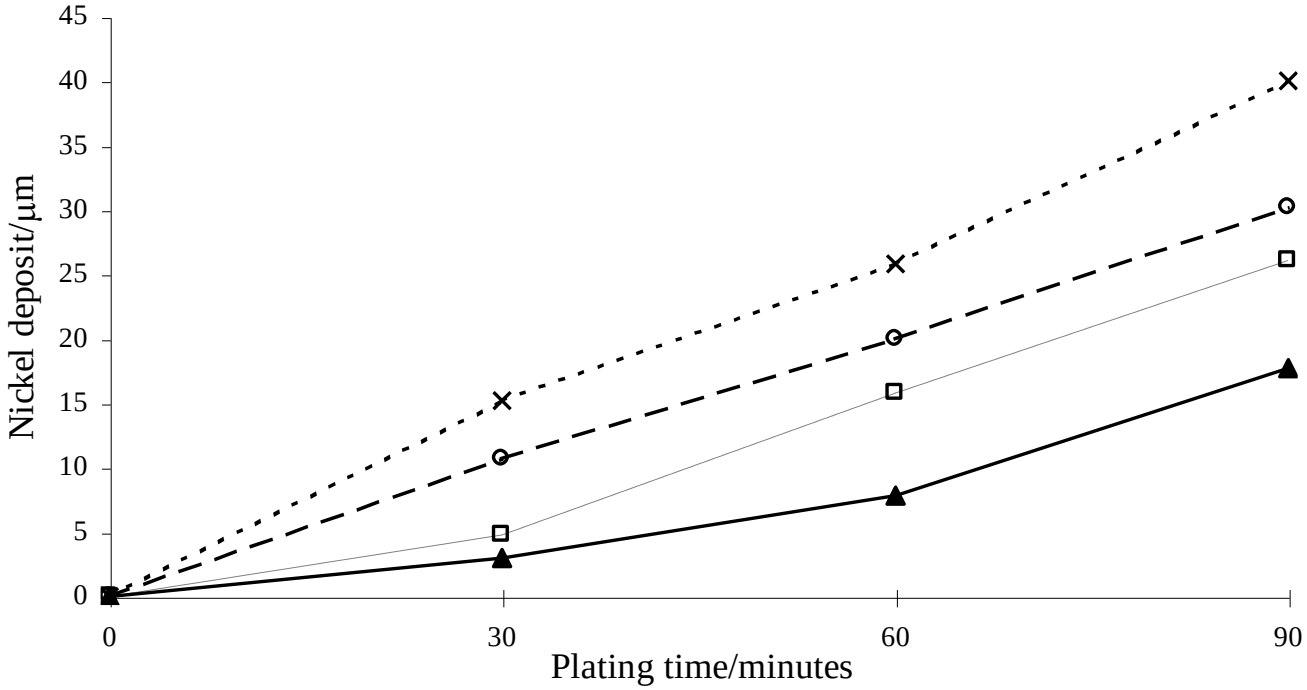
45
40
35
30
25
20
15
10
5
0
Nickel deposit/µm
0
30
60
90
Plating time/minutes

Figure 2

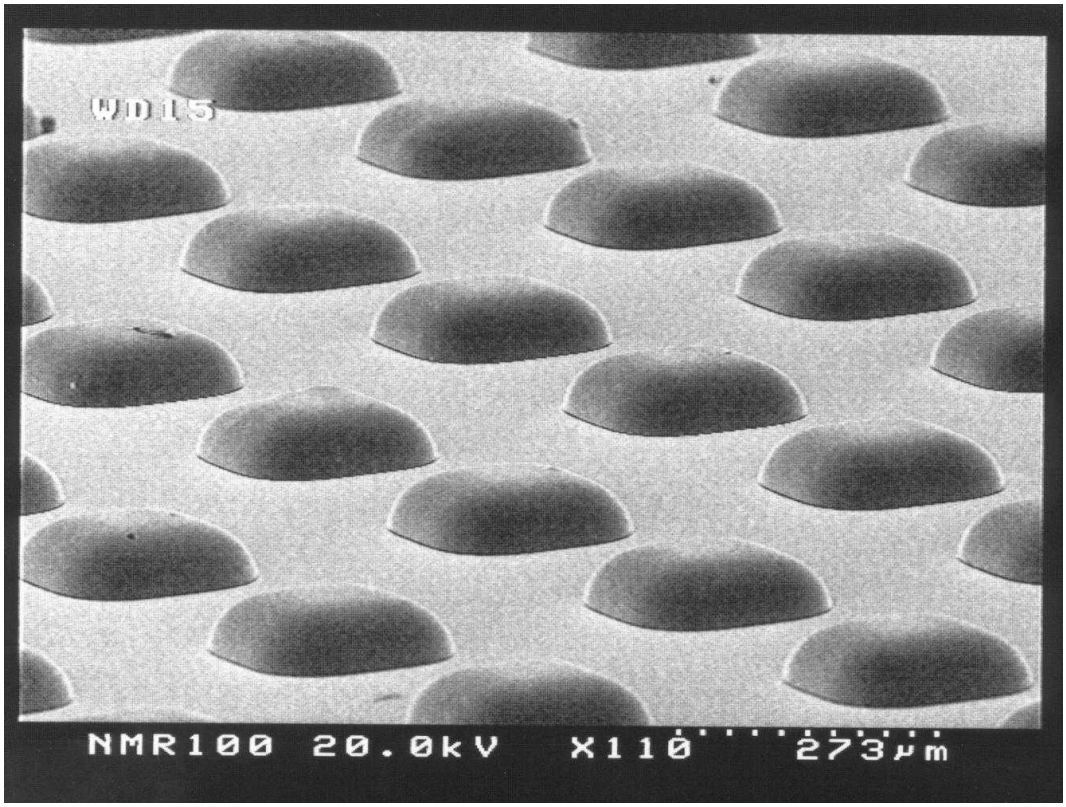

Figure 3

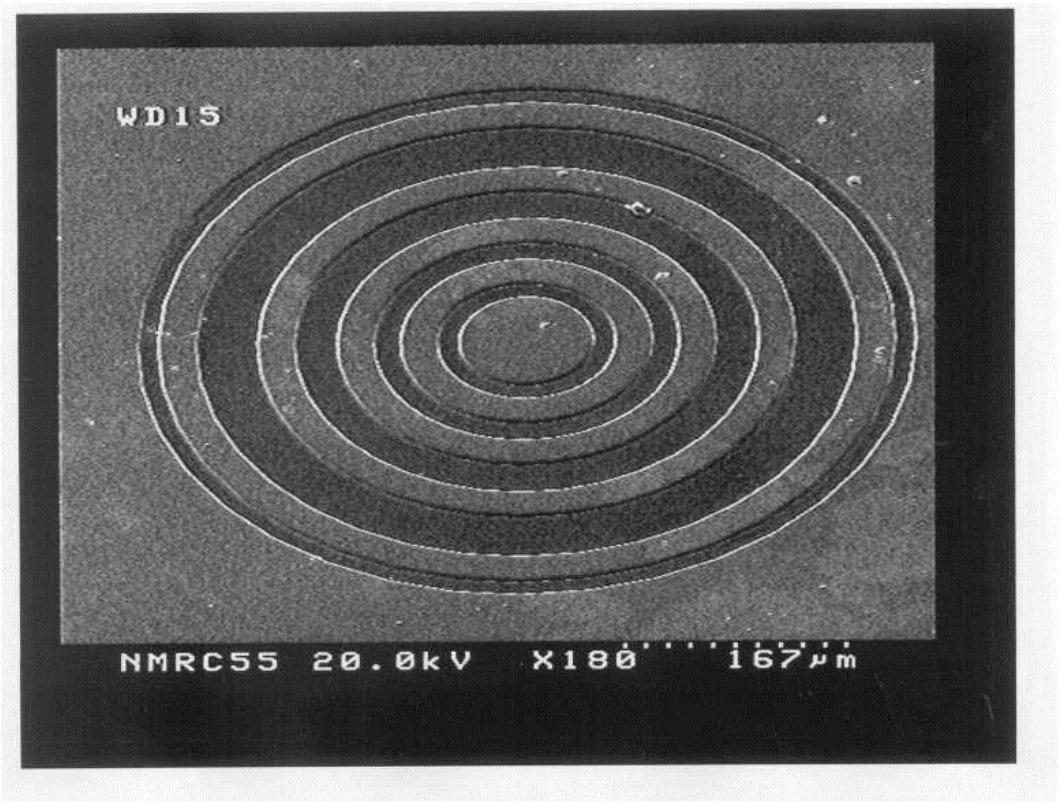

Figure 4(a)

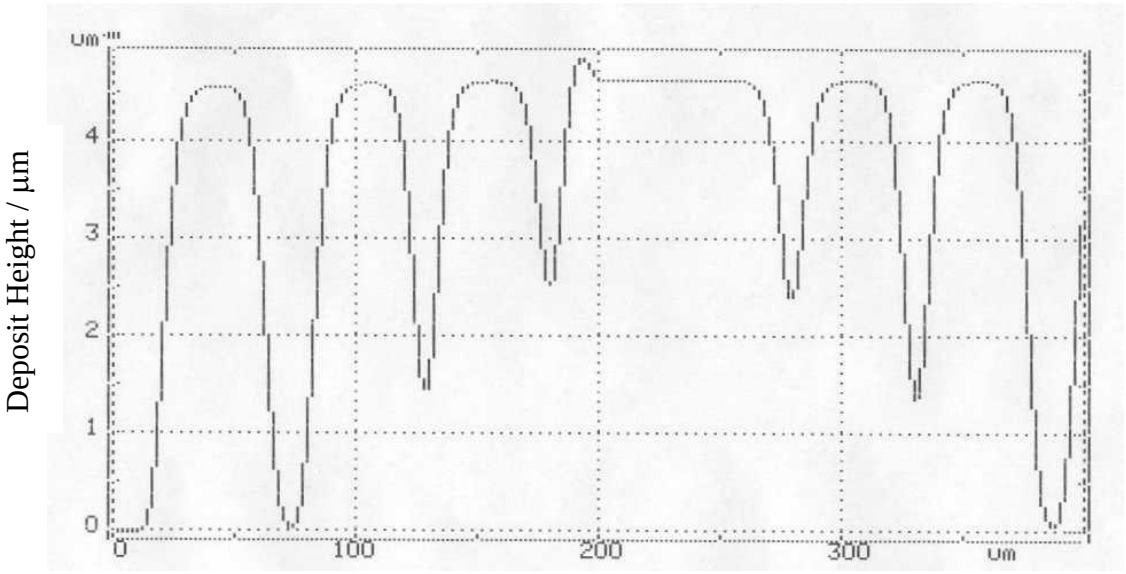
Deposit Height / μm
Substrate dimension / μm
0
1
2
3
4
0
100
200
300
μm

Figure 4(b)

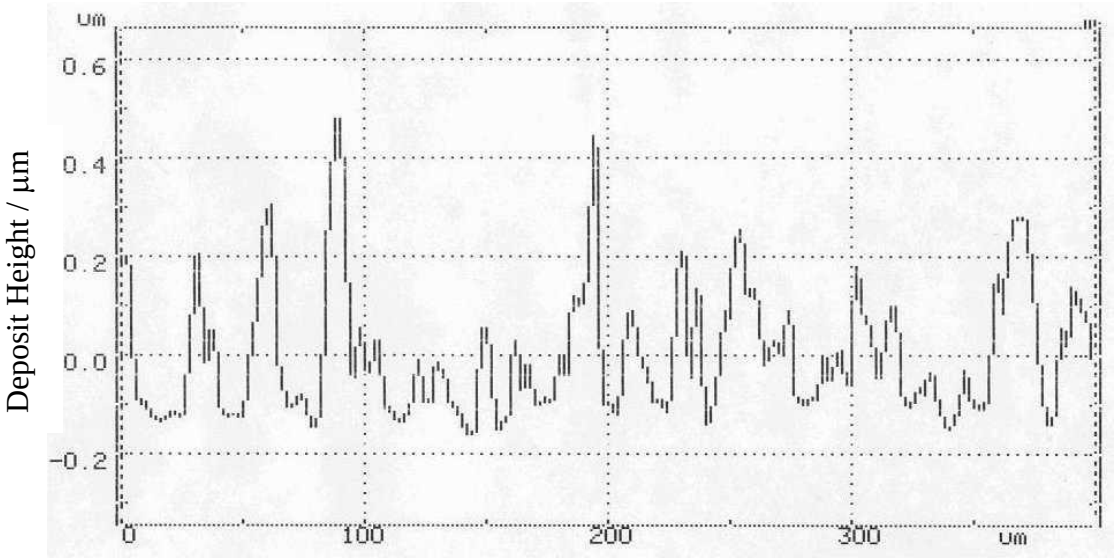
Deposit Height / μm
0.6
0.4
0.2
0.0
-0.2
0
100
200
300
Substrate dimension / μm

Figure 5

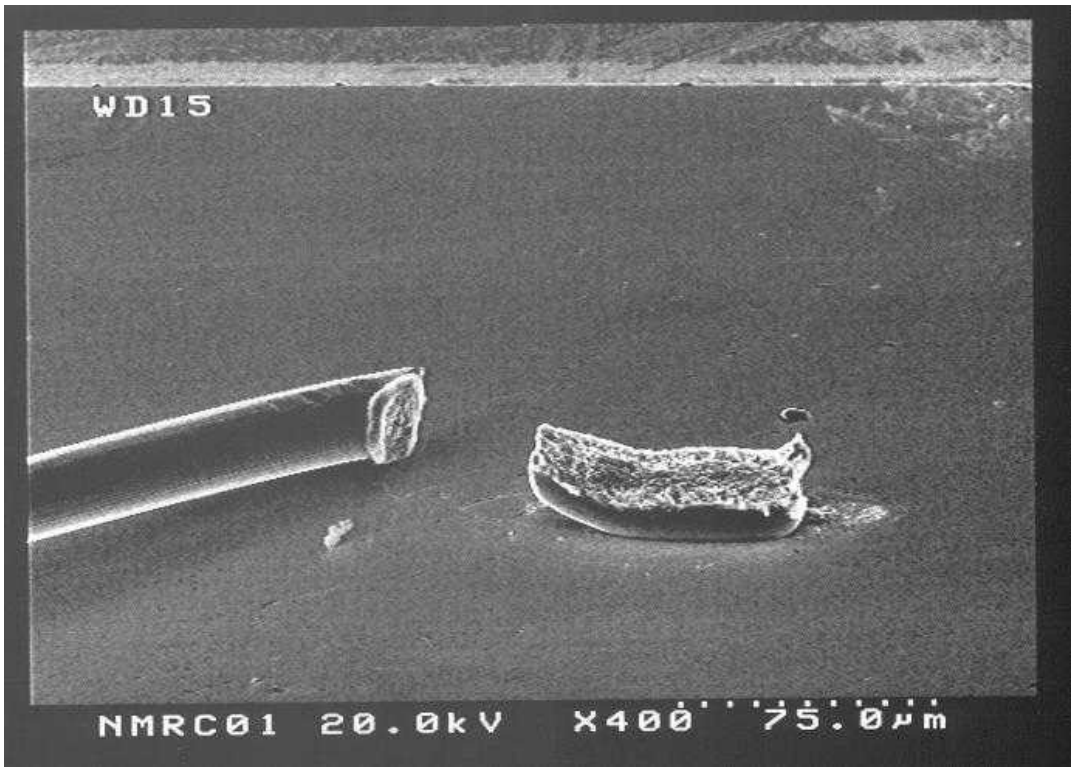

Figure 6

Bath Name	NMRC	Alfachimici Niflex SMT	Canning Nimax SB	Enthone Enplate Ni 865
Reducing agent	Hypophosphite	Hypophosphite	Hypophosphite	Hypophosphite
% P content	6 – 10	8 - 10	7 – 12	6 - 8
Operating Temperature ^{o}C	82-92	83 - 87	85 – 93	82 – 92
pH range	4.2 – 4.6	4.6 - 5.0	4.8 – 5.3	4.6 - 5.0
Deposition Rate μm/hr	8 - 20	10 - 15	15 - 25	15 – 23

Table 1

Activation Type	NMRC Ni	Alfachimici Niflex SMT	Enthone Enplate Ni-865	Canning Nimax SB
Palladium	8.1	16	25.8	19.8
Shipley Niposit 468	4.2	14	20	19.2
Borane solution	3.2	5.1	7.8	10.8
Plating solution activation	3.9	5.6	15.8	16
Manufacturers quoted ranges	-	10-15	15-23	15-25

Table 2

Electroless Nickel Solution	Deposition Duration minutes	Activation Type	Deposit Height Range µm	Mean Deposit Height µm	Standard Deviation µm
Enthone Enplate Ni-865	180	Pd	64.2 – 65.8	65.3	0.5
Enthone Enplate Ni-865	180	Shipley Niposit 468	57.1 – 61.6	58.9	1.3
Enthone Enplate Ni-865	180	Solution Activation	40.0 – 41.4	40.9	0.3
Alfachimici Niflex SMT	90	Pd	22.7 – 23.8	23.2	0.4
Alfachimici Niflex SMT	90	Shipley Niposit 468	21.3 – 22.0	21.6	0.2
Alfachimici Niflex SMT	90	Solution Activation	24.5 – 25.8	25.4	0.4

Table 3

Nickel bond layer thickness μm	Copper to copper bond strength gm	Copper to nickel bond strength gm	Nickel to nickel bond strength gm
1.4	12.5	11.6	9.3
3.0	10.5	10.3	10.3
4.7	10.5	10.4	11.0
6.7	10.4	8.7	10.2
Mean bond strengths (standard deviation)	11.0 (0.9)	10.2 (1.0)	10.2 (0.6)

Table 4

Sample No.	Plating Duration minutes	Deposit Thickness μm	Adhesion tape test	% failed bonds	Mean bond strength gm
1	10	0.2	passed	0	9.4
2	15	0.3	passed	55	4.9
3	30	0.8 – 1.2	passed (after anneal)	100	-

Table 5