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# Zincate-free, electroless nickel deposition on aluminium bond pads.

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## Abstract.

A zincate-free electroless nickel deposition on aluminium bond pads is investigated. A three step, etch, rinse and electroless plating is demonstrated for deposition on aluminium bond pads patterned with polyimide. The chemicals used are compatible with this dielectric material. The deposition has been achieved with good selectivity, uniformity and deposition rate at 40 x 40 μm square aluminium bond pads. The adhesion and contact resistance were also determined and improved through anneals in the range 200 to 400°C for one hour. The optimised condition for adhesion and contact resistance was an anneal at 400°C. The combination of a nickel hypophosphite reducing agent and the additives used leads to an active plating bath in the early stages of deposition, by comparison with commercial solutions, and hence good coverage of the aluminium bond pad using the simplified process.

## Introduction.

Electroless nickel deposition on aluminium usually requires a series of pretreatment steps to ensure good quality deposits. The pretreatments are necessary to remove the native surface oxide film on the aluminium and to prevent reoxidation of the etched aluminium. The most common pretreatment employed in industry [1] and more recently in chip bump processing [2-6] is the zincate treatment which involves immersion of the aluminium substrate in a concentrated sodium hydroxide based solution containing zinc ions which removes the oxide and deposits a protective zinc layer. It is usually necessary to repeat the process to obtain the best quality coverage. Upon immersion in the electroless nickel plating solution the zinc dissolves and is replaced by nickel ions which initiates the autocatalytic deposition of nickel directly at the aluminium surface. In microelectronics applications this process has some potential drawbacks including process complexity and the exposure of the substrate to undesirable metal ion contaminants such as zinc. For these reasons alternative activations of the aluminium substrate for electroless nickel deposition have been investigated, such as, HF etching [7] deaerated rinsing solutions and displacement nickel deposition or activation by dimethyl amine borane (DMAB) solution [8] and laser irradiation of the aluminium to remove anodically formed oxide [9]. An additional process step, the deposition of a thin Ni-B base layer from alkaline solutions, has also been required in some cases [4,8] before deposition from the more common hypophosphite could take place. This paper describes a simple etch, rinse and plating process for the selective deposition of electroless Ni-P bumps on aluminium bond pads for use in flip chip assembly.

## Experimental.

All experiments were performed in glass beakers with magnetic stirring at 100rpm. The plating solution was heated on a hotplate with a teflon coated temperature probe to maintain a constant temperature. The pH was adjusted using ammonium hydroxide to the required value at room temperature and then heated to the operating temperature. Teflon substrate holders were used. The substrates were patterned aluminium (1.5 μm thick) bond pads (40 x 40 μm) deposited using an Endura AMAT 5500 PVD deposition tool. The patterning material was 3 μm thick polyimide (PI) The deposit selectivity and morphology were analysed using a Hitachi S-400 field effect scanning electron microscope (SEM) with a PGT IMIX Energy Dispersive X-ray (EDX) system with intensity correction for elemental analysis of deposit composition and uniformity. Deposit height and uniformity was determined using a Tencor Alpha-Step 200 surface profilometer and correlated with data recorded on the SEM. Samples were annealed under a nitrogen ambient in a solder reflow over (SRO 702) by ATV Technology Inc. The adhesion of 40 μm high nickel bumps was measured using a Dage BT 24 shear tester from Dage Precision Industries Inc. CA. In these tests nickel bumps were sheared from the aluminium substrate using a 100 μm tool head which has a lead edge perpendicular to the substrate and travels parallel to the substrate at a rate of 500 μm/s at a height of 5-10 μm. The force to shear the bump recorded is the average of 15 tests for each substrate.

An alkaline etch composed of 50mls each of $H_2O_2$ and $NH_4OH$ of the concentrates (30% semiconductor grade, supplied by Ashland Chemicals, Ohio) in 1 litre of deionised water was used to clean the aluminium surface and remove the oxide layer. An optimised etch time of 30 seconds removed 0.3μm of aluminium, the native aluminium oxide was removed and the surface was slightly roughened. The use of an alkaline etch step in the plating process was critical to the activation of the aluminium bond pads to electroless nickel plating. After etching, the wafer was immediately rinsed in propan-2-ol. This solvent rinse was used, rather than an aqueous rinse, to help prevent the re-oxidation of the fresh aluminium surface. The sample was transferred directly from the solvent to the plating solution. The plating bath operates at a temperature of 87-90ºC and the boiling point of propan-2-ol is 84.2ºC, thus any propan-2-ol remaining on the aluminium pads after the solvent rinse evaporates on immersion of the samples into the plating bath. An electroless nickel bath formulated from its constituents, Table 1, and three commercial baths were examined. Details for the commercial solutions have been described earlier [10] All baths were based on a hypophosphite reducing agent and operated at a pH of 4.0 to 5.0. The bath in table 1 was also designed to be sodium ion free utilising nickel hypophosphite as the reducing agent. This electroless nickel bath afforded selective uniform plating on the aluminium bond pads. The commercial electroless nickel baths were not sufficiently active to initiate nickel plating on the aluminium surface using the simplified alkaline etch and solvent rinse process.

## Results and Discussion.

### *Plating process:*

Nickel bumps were selectively deposited using a simple process that did not require the use of an additional metal deposition step such as occurs in the standard zincate process. The plating process utilised consisted of an etch step and a solvent rinse prior to plating. This metal deposition method has a number of advantages over other aluminium activation processes such as zincation or palladium activations. Firstly the sample is not exposed to additional species such as zinc, sodium or palladium, and secondly, the process is very selective and the rear of the wafer is not plated.

Initial plating experiments using the acidic nickel bath operating at a pH of 4.2 and operating temperature of $85^{o}$C afforded nickel plating at a typical rate of 8 µm/hour. Increasing the operating temperature to $90^{o}$C and solution pH to 4.6 increased the deposition rate to 20 µm/hour. Figure 1 illustrates a selectively plated array of 58µm high nickel bumps on a wafer that was plated in the acidic nickel bath for 3 hours. The plating uniformity of the electrolessly deposited bumps is indicated in Table 2 which lists the mean and standard deviation for 30 sites on the substrate. The data indicates that the deposit uniformity is maintained over extended deposition times.

*Adhesion:*

In electroless plating, deposition commences autocatalytically only on the patterned aluminium of the bond pad. Additional photolithographic patterning is not required. This is a significant advantage of the electroless process. However, the deposit grows both vertically and laterally at the same rate as shown in the cross sectional SEM image of figure 1b. The lateral growth causes the bump to spread onto the passivation surrounding the aluminium bond pad. The adhesion of this lateral plating to the passivation, in this case polyimide (PI), may be low. In electrolytic metallisation of bond pads, a metal seed layer is deposited which covers both the aluminium bond pad and the passivation. Photolithography is used to constrain bump growth to the required areas over the bond pads and the bump material is deposited only over metal which provides adequate adhesion. The nickel to aluminium adhesion required from electrolessly plated deposits therefore must be greater than the comparable bump plated by electrolytic means. To improve the bump-wafer adhesion with electroless plating, either the nickel to passivation or the nickel to aluminium adhesion, or both, must be increased.

Chemical and physical modification of the PI prior to plating was studied as a method to increase the Ni-PI adhesion. The factors examined in order to increase the Ni-Al adhesion included improving the plating process and annealing the samples after plating. Initial bump shear strength tests indicated that the bump to wafer adhesion strength was 35g per pad for the 40 x 40µm metal connection, when the nickel was deposited at pH 4.2 and a plating bath temperature of 85$^o$C. The results of the bath operating conditions and substrate treatments which lead to a large increase in nickel to wafer adhesion are given below in Table 3.

The physical treatments to roughen the polyimide surface included an oxygen plasma ash and abrasion of the surface using silicon carbide paper. The SEM image in Figure 3 illustrates the surface of the polyimide following abrasion using silicon carbide paper. All treatments that roughen the polyimide surface lead to an increase in adhesion shear strength. Oxygen plasma etching of the polyimide prior to plating afforded the largest shear strength increase; a value of 130g/pad was measured which compares very favourably with shear strength values quoted for electroless nickel bumps [5]. Chemical treatments included alkaline and acid solutions and an n-methyl-pyrrolidinone (NMP), dip. NMP is used to strip polyimide at elevated temperatures, and softens the material at lower temperatures. Chemical treatment of the samples prior to plating did not, however, lead to an increase in the bump-wafer adhesion.

To further improve the overall adhesion, the effect of annealing on the plated die was also examined. Samples were annealed at a range of temperatures between 200 and 400ºC. Annealing was found to increase the nickel to aluminium adhesion with higher anneal temperatures affording the greatest increase in adhesion. Shear strengths of 170 g/pad were measured when samples were annealed at 400ºC in an oxygen free environment for one hour again indicating good adhesion for the small pad size.

SEM analysis was also used to examine the aluminium bond pads of plated samples where the nickel bumps had been removed during shear testing. Where samples had been annealed the surface of the aluminium was rougher than samples that had not been heat-treated. No nickel was detected by EDX at the bond pad following shear test. This suggests that annealing the samples causes a localised interaction between the nickel and the aluminium bond pads. This interaction probably accounts for the increase in adhesion upon annealing. Figures 4(a) and 4(b) are SEM images of aluminium bond pads for plated samples where the nickel bumps have been removed by shear testing. The sample in Figure 4(a) was not annealed while the sample in Figure 4(b) has been annealed at 400ºC prior to shear testing.

### *Auger analysis:*

Auger depth profiling of a series of samples as plated and after anneals at 200, 300 and 400ºC did not show significant interdiffusion at the Ni/Al interface. The profiled samples were plated with a thin nickel deposit (~ 5µm thick). Auger spectra were acquired affording detailed information on the composition of the nickel/aluminium interface. Comparing the spectra of the sample as-plated and annealed at 400$^{o}$C showed no detectable variation in peak shape or shift at the interface areas. This suggests that the oxidation states of nickel and aluminium do not change around the interface region and thus intermetallic compounds are not being formed. Figures 5a and 5b illustrate the depth profiles of atomic composition of an as-plated sample and a sample annealed at 400ºC. In the spectra the Al is observed at the right hand side of the spectra, the nickel and phosphorous are seen on the left hand side and the oxygen signal is at the bottom of the spectra. These results were supported by EDX line scans which did not indicate a significant concentration change at the interface following an anneal at 200 to 400$^{o}$C.

*Resistance measurements:*

The contact resistance between the deposited electroless nickel and the underlying aluminium of the wafer was investigated using two point probe resistance measurements. These measurements were carried out on bumped wafers that had not been annealed and on samples that were annealed at temperatures of 200, 300 and 400ºC. Test structures (figure 6) measured on the substrate involved multiple nickel-aluminium daisy chained contacts. Using this structure, the resistance of a large number of Ni/Al interfaces and Al links can be measured at one time with a two probe system.  Measurement at this test structure provide a better representation of the resistance of the system as the interfaces are not influenced by the pressure applied to the deposit during probing.

The resistance values measured on a series of samples are illustrated in Figure 7. The resistance measured versus the number of Ni/Al interfaces is plotted for a series of samples that were measured as-plated and annealed at 200, 300 and 400°C. All the resistance values measured indicate a low Ni/Al contact resistance per bond pad. Annealing the samples affords a reduction in resistance values at the Ni/Al interface. In figure 7 below a dramatic decrease in resistance was observed when samples were annealed at 400°C. Based on previous analysis [11] the crystallisation of the electroless nickel deposit may be the factor contributing most to this result.

Based on the plating observations and deposit analysis it is proposed that the peroxide/ammonia etchant removes the oxide at the surface of the aluminium as indicated by the 0.3 μm decrease in aluminium pad height following this treatment. The etched aluminium surface is protected from reoxidation by immersion in the non-aqueous rinse solvent which is similar to the protection afforded by zinc in the standard zincation process. This solvent also protects the aluminium surface during transfer to the nickel plating bath and during the initial seconds of immersion in that bath. The zincate process affords a more durable protection and is better suited to the full range of substrate dimensions. The solvent protection described in this work protects the relatively small pad area adequately during the timescale of removal from the solvent rinse and immersion in the plating bath. Once in the plating solution the exposed aluminium surface is most likely involved in a displacement reaction with the nickel ions, again in a mechanism similar to that which occurs following zinc dissolution in the zincate process, given the potential difference between the aluminium dissolution and nickel ion reduction reactions. The plating bath used is more active for nickel deposition at the operating pH of 4.6 and temperature of 90°C (20 μm/hour achieved) than at a pH of 4.2 and temperature of 85°C (8 μm/hour achieved) and more active than commercial solutions which did not yield deposits using this technique. This may be due to the lower additive content for the bath described in this work which can yield deposits at 20 μm/hour from the zincate-free process. Therefore, it would appear that the critical displacement and subsequent autocatalytic deposition that occurs in the early stages (0.3 μm/minute expected by extrapolating from the long term deposition experiments) does so in a uniform manner across the bond pads at a high rate before the aluminium reoxidises. In addition to the increased deposition rate under the optimised plating conditions, shear test analysis indicated that the nickel has better adhesion to the aluminium when the nickel deposited at a higher rate. This most likely results from direct nickel to aluminium contact which occurs at a substantially oxide free surface.

## Conclusions.

A zincate-free route for electroless nickel direct deposition on aluminium bond pads has been demonstrated. This technique is significantly simpler, requiring only three steps, than the standard zincate process and does not require the use of hazardous chemicals, such as HF, employed in some cases as an alternative to the zincate treatment. It also affords selective deposition which may not be achieved using Pd or other such activating solutions to assist the initial deposition on the aluminium. The deposition has been achieved with good selectivity, uniformity and at a relatively high deposition rate of 20 μm/hr at 40 x 40 μm square aluminium bond pads. For flip chip applications where the electroless nickel acts as an under bump metallurgy, adhesion and contact resistance are significant factors. These have been determined and optimised through anneals in the range 200 to 400°C for one hour. Similar selective deposition was not achievable with commercial plating solutions using this three step process. It is suggested that the combination of the active plating bath with few additives, comprising a nickel hypophosphite reducing agent, leads to a more active plating bath in the early stages of deposition and hence good coverage of the aluminium bond pad using the simplified process described above.

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**Table 1. The composition of the electroless nickel bath.**

| Chemical | Molarity |
|---|---|
| Nickel sulphate | 0.05 |
| Ammonium sulphate | 0.25 |
| Nickel Hypophosphite | 0.13 |
| Lactic acid | 0.22 |
| Calcium succinate | 0.01 |
| pH | 4.0-5.0 |
| Temperature | 85 – 95$^o$C |

**Table 2.** **Nickel bump height uniformity.**

| Sample | Number of measurement sites | Mean bump height/μm | Standard Deviation /μm |
|---|---|---|---|
| 1 | 30 | 52.52 | 1.61 |
| 2 | 30 | 51.90 | 2.40 |

**Table 3. Adhesion data for nickel deposits on substrates subjected to listed treatment.**

| Treatment | Deposit height /µm | Shear strength /g per pad | Standard Deviation /g per pad |
|---|---|---|---|
| Untreated sample | 40 | 66.0 | 11.1 |
| Oxygen Plasma etch | 45 | 130.1 | 8.3 |
| Abrasion 4000 grit SiC | 30 | 84.8 | 4.2 |
| Abrasion 2500 grit SiC | 30 | 89.6 | 5.1 |
| Abrasion 1200 grit SiC | 30 | 95.7 | 4.0 |
| Anneal 200ºC | 40 | 61.8 | 7.2 |
| Anneal 300ºC | 40 | 95.2 | 21.1 |
| Anneal 400ºC | 40 | 173.2 | 30.7 |

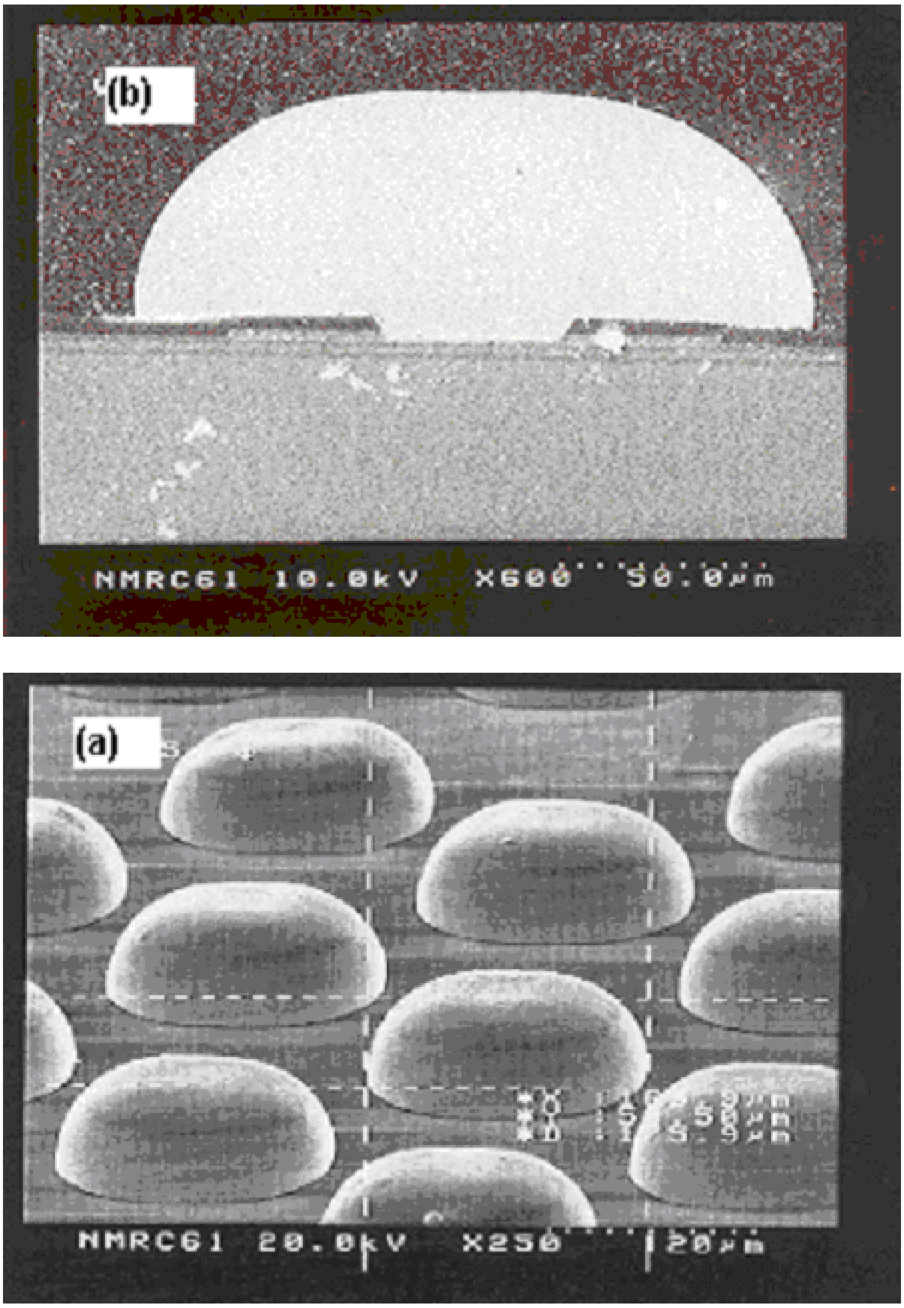

Figure 1. Selective electroless nickel bumps deposited in 3 hours plating on aluminium bond pads 40 x 40 µm (a) SEM image of nickel bump array and (b) cross section of a nickel deposit.

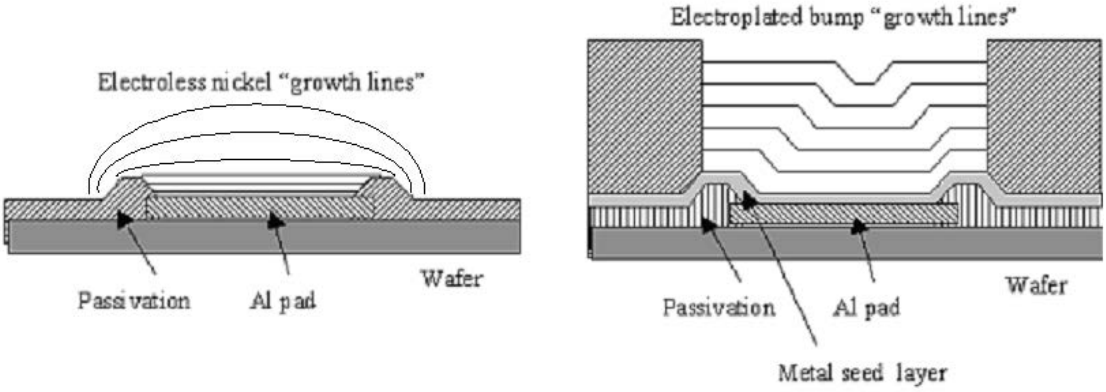

Figure 2. Growth lines for electroless and electrolytic deposits on aluminium bond pads.

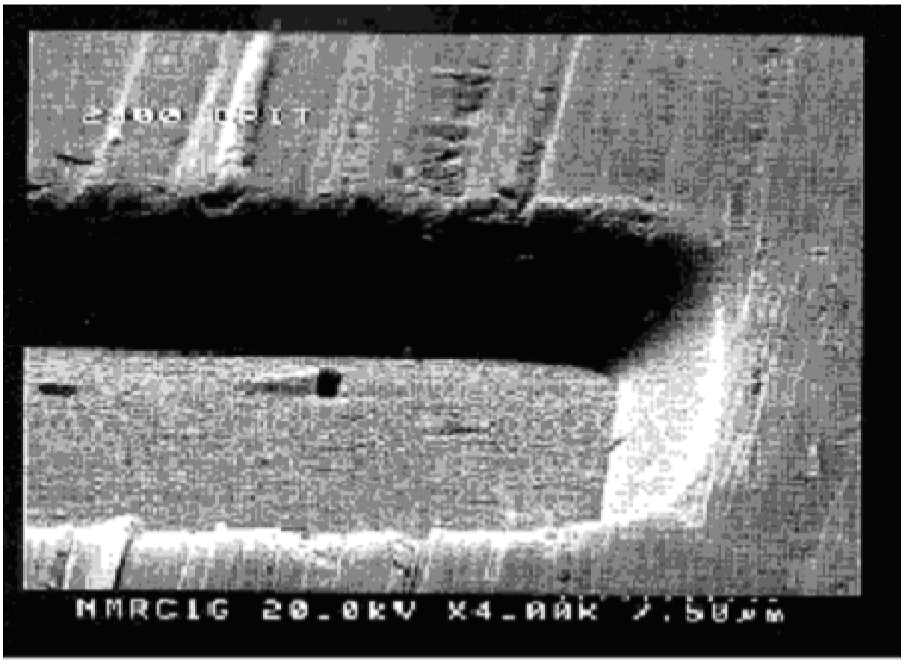

Figure 3. SEM image is of an aluminium bond pad and polyimide after abrasion using 4000 grit silicon carbide paper.

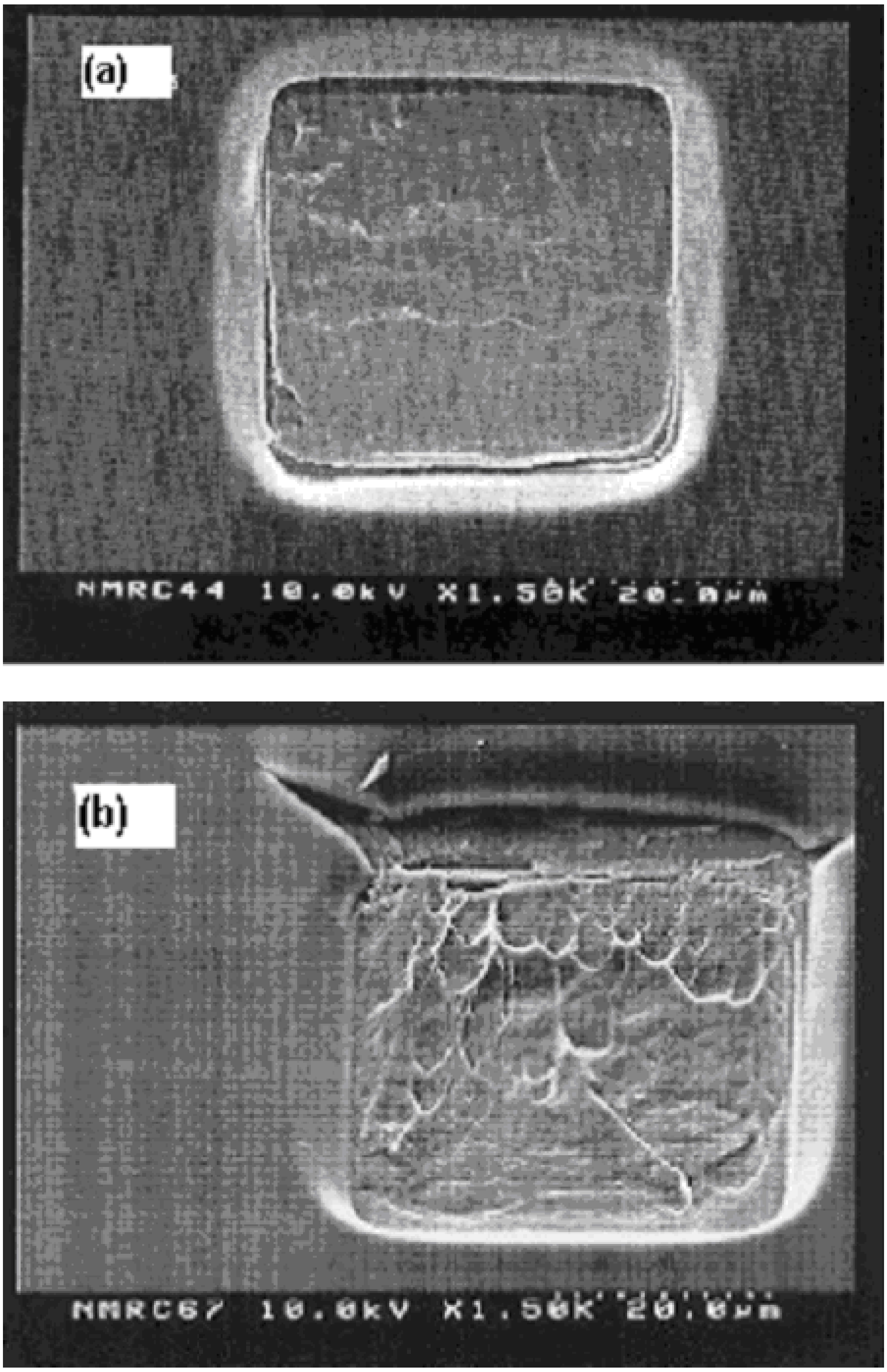

Figure 4. SEM images of aluminium bond pads of plated samples where the nickel bumps had been removed. (a) no heat treatment and (b) annealed at 400°C prior to shear testing. No nickel was detected at the remaining aluminium of the bond pad.

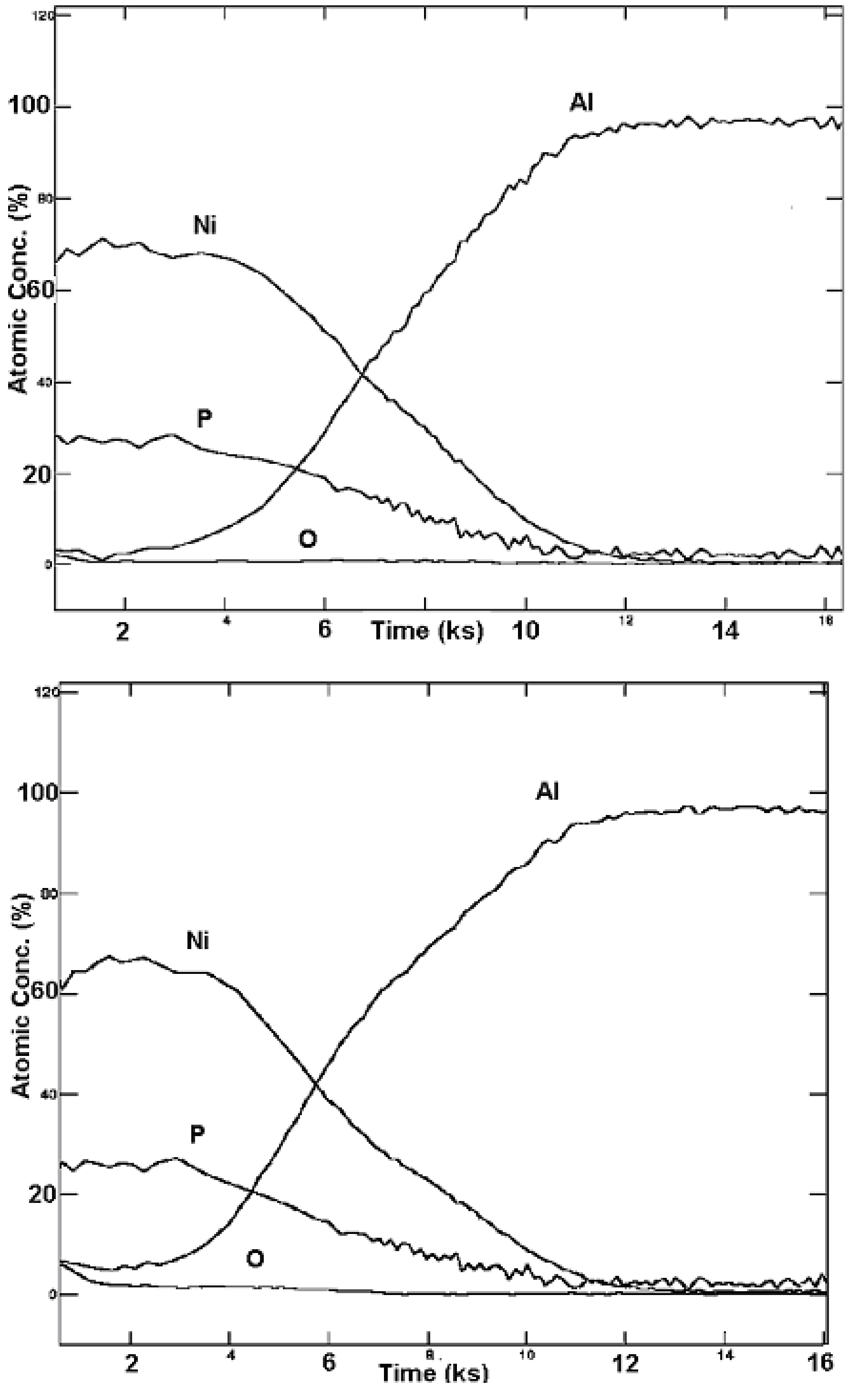

Figure 5. (a) Auger depth profiles of atomic composition of the Ni/Al interfaces of samples as plated and (b) after annealing at 400ºC.

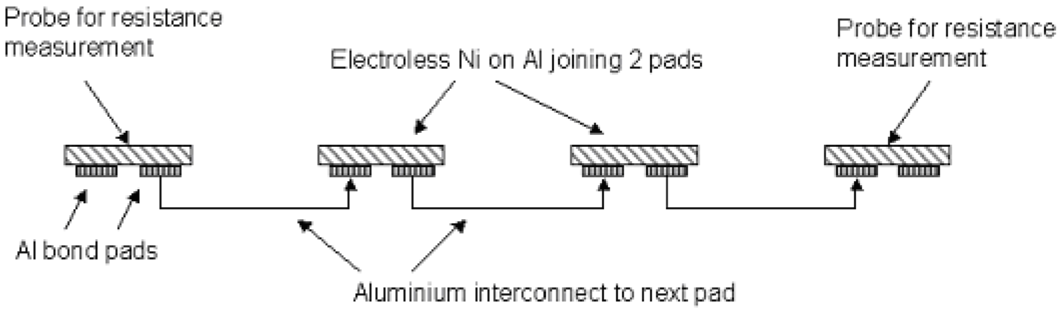

Figure 6. Schematic of the daisy chain layout with aluminium pads connected along the chain though electroless nickel deposit. Probing for resistance is only performed at the start and end of chain permitting the determination of the resistance of a series of nickel/aluminium interfaces.

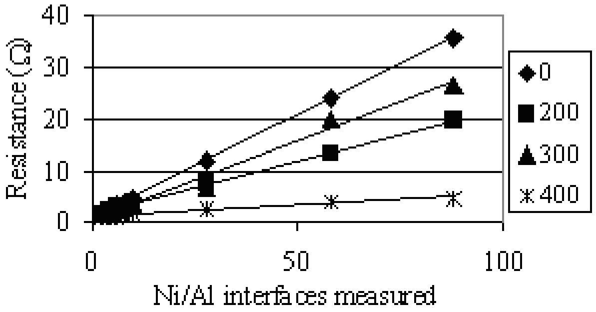

Figure 7. Resistance measurements versus Ni/Al interfaces. Samples as-plated and after annealing at 200, 300 and 400ºC.