Main Impact Factors on Internal Stress of Electroless Deposited Copper Films

Tobias Bernhard,[a]* Sebastian Zarwell,[a] Frank Brüning,[a] Ralf Brüning,[b] Tanu Sharma, [b]
Atotech Deutschland GmbH, Erasmusstraße 20, D-10553 Berlin, Germany.
Phone:+49 (0)30 34985 557. Fax: +49 (0)30 34985 618. E-mail: tobias.bernhard@atotech.com
[b]*Physics Department, Mount Allison University, Sackville, New Brunswick, Canada E4L 1E6*

Abstract

Electroless deposition of thin Cu layers is one of the crucial steps during the manufacturing of printed circuit boards (PCBs). Electroless Cu serves as a conductive seed layer on nonconductive substrate material (epoxy, polyimide, glass, etc.) for the subsequent deposition of electrolytic Cu. In through holes and blind micro vias a dense and well adhering seed layer is essential to assure functionality and reliability of the final product. Adhesion of electroless Cu layers on dielectrics is mainly attributed to mechanical anchoring. Therefore surface roughness of the substrate enhances adhesion. However, to comply with the continuing trend towards miniaturization, smoother dielectrics are employed to allow reduced line and space dimensions. Recently introduced novel substrate materials are prone to spontaneous delamination failures (blistering) of the electroless layer during deposition. A higher Ni content in electroless Cu electrolyte prevents this delamination failure by increasing the internal tensile stress in the Cu layer. This effect is achieved by suppressing Cu self-diffusion through the incorporation of small amounts of Ni in the grain boundaries and the grain boundary junctions. Apart from the Ni-concentration in the electroless Cu-bath, here we investigate additional influence parameters on the internal film stress, e.g. the concentration of NaOH, cyanide and solution flow of the bath. Some of these parameters modify the internal film stress indirectly by influencing the amount of codeposited Ni. This provides a first insight into mechanisms of Ni-codeposition during electroless Cu plating.

Key words

electroless copper, internal stress, Ni-codeposition, delamination failure

I. Introduction

The PCB build-up process is simply described by alternating stacks of organic insulation layers and conductive metals. The Semi-additive process (SAP) is widely used to form metallic conductive patterns which are electroplated on the electroless deposited copper (Cu) seed layers on top of insulating organic layers [1]. Recent advances are increasingly required to provide smoother and thinner PCB substrates for the highly integrated electronic devices. In addition, new organic materials are being used such as polyimide (PI), liquid crystal polyester (LCP) and bismaleimide triazine (BT) resins, because of their superior performance as insulating layers at high temperatures and high signal frequencies [2]. As plated structures become smaller and substrates smoother, film adhesion is increasingly problematic. Warpage, delamination and blisters are well-known failure modes due to insufficient control on stress and adhesion, thus stress data are becoming part of industrial process specifications. For electroless copper a moderate tensile stress is essential for the film substrate adherence. The experimentally observed appearance of blisters is explainable in a semi-quantitative concept of critical compressive stress [3]:

$$\sigma_{crit} \approx PS / d_{Cu} \qquad (1)$$

, where d_{Cu} is the thickness of the Cu film and *PS* is the peel strength with unit force/length. If the internal film stress during deposition, rinse-induced cooling and annealing is lower (more compressive) than σ_{crit}, then blistering of electroless Cu is observable.

Nickel, initially added to the electrolytes in order to improve deposition speed, prevents compressive stress. A small amount of metallic Ni is incorporated mainly at the grain boundary junctions in the Cu film [4,5]. How codeposited Ni influences the internal stress in electroless Cu films is well investigated (see details in section II.A). Less is known about the deposition process of Ni and especially the interplay with components and conditions in the electroless Cu electrolyte.
Fig. 1 shows the internal stress of an as-growing electroless Cu layer (at a thickness of 0.7 µm), as a function of Ni concentration for two different electroless Cu baths

(abscissa for Bath B in blue on top of the graph). The internal stress in the Cu layer was measured by in-situ X-ray diffraction on ABS (Acrylonitride-Butadien-Styrene) substrate [6].

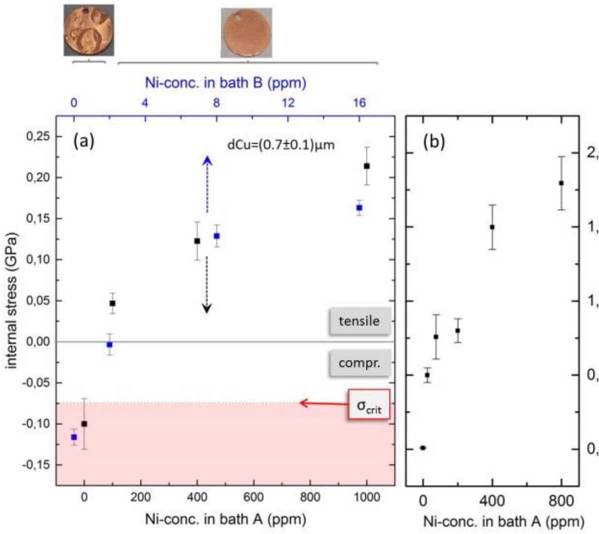

Fig.1) a) Internal stress as a function of Ni concentration for two different electrolytes A (in black) and B (in blue). The Ni-conc. of bath B is related to the blue abscissa. b) fraction of incorporated Ni by the Ni-conc.in bath A

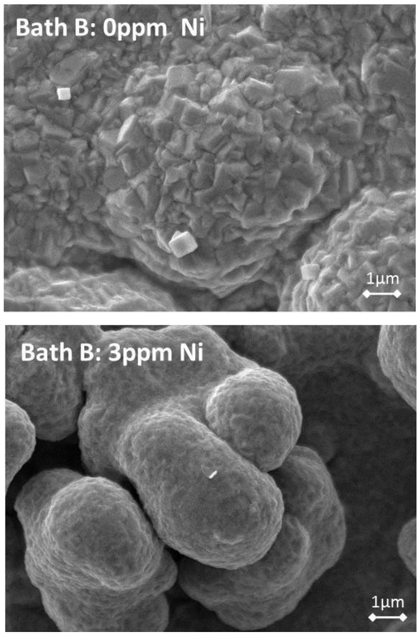

Fig.2) Surface of 1µm thick electroless Copper films deposited in bath B without Ni(top) and with 3ppm Ni

A and B are tartrate based baths with different nitrogen-sulfur stabilizer systems. Experimental conditions, as temperature, deposition rate and liquid flow are similar for these electrolytes. In both baths without Ni, the copper films show stress below the critical compressive stress σ_{crit} (calculated from (1) with estimated PS=0.5 N/cm), in conjunction with the appearance of blister failures (insets in Fig.1). For bath A an increase of Ni-conc. up to 400 ppm is necessary to ensure a tensile stress of 0.12GPa in the film. This is accompanied by an incorporated Ni fraction of about 1.5w%. Surprisingly, for bath B the same rise of tensile stress is obtainable with only 8ppm Ni in the bath. Moreover, adding a trace of Ni (only 3ppm) in bath B (this corresponds to max. 0.13w% incorporated Ni), the grain size of the copper deposit is substantially reduced (Fig.2). From this observation it is evident that Ni-codeposition depends critically from the bath-composition and is a crucial parameter to affect characteristics of Cu-growth.

In this context, the subject of this work is to find out main impact factors on Ni-incorporation during electroless Cu-deposition and how this affects the internal film stress of the deposit.

II. Experimental

A. Methods

The time-evolution of average stress in copper films was determined based on a substrate curvature technique, known as in-situ Deposit Stress Analysis (DSA) [7]. The experimental set-up is depicted in Fig.3:

The Palladium activated samples were mounted on an optical bench in front of a camera. The electroless plating solution was held in a transparent Plexiglas container. The container with the plating solution was raised to immerse the test strip, and photographs were taken before, during and after plating. Two kinds of substrates were used: Metal test strips made from Ni–Fe (alloy 42, 38 µm) were purchased from Specialty Testing and Development Co., York, Pennsylvania. The ABS test strips were cut from 0.5 mm thick ABS sheet (CS Hyde Company, Lake Villa, Illinois) to the same shape and size as the metal strips. Details for pretreatment of ABS-test strips and determination of bending constant K can be found in [7]. The strips have two legs that are varnished on opposite sides, such that the Cu film grows only on one side of each leg, and film stress will bend the legs in opposite directions. By monitoring the bending f of the strips the internal film stress can be derived by:

$$\sigma = 2f \cdot K / 3d_{Cu} \tag{2}$$

The final thickness of the Cu film d_{Cu} is measured afterwards via mass-gain (metal strips) or Cu-titration (ABS). For the purpose of this analysis we assume that the films grow at a constant rate during plating.

To determine the Ni-incorporation the deposited Cu films on ABS or FR4-substrates were measured by a X-ray fluorescence spectrometer (Fisherscope XDV-SDD) by using the ratio of Ni-Kα and Cu-Kα signal. The detection limit of this set-up is lower than 0.2w%.

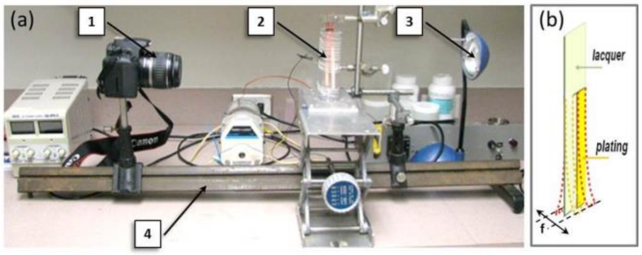

Fig.3) a) Set-up to measure internal film stress during electroless Cu deposition. The test strip is positioned in a transparent container (2), filled with electroless Cu solution, the container is aerated and heatable and illuminated from the back side (3). Photos of strip bending were automatically taken by a camera (1). The setup is mounted on an optical bench (4) b) scheme of test-strip bending during deposition

B. Impact of incorporated Ni on internal stress

Fig.4) shows the typical internal stress evolution for electroless copper deposited in an electrolyte without Ni (black curve) and with Ni (red squares), measured by in-situ DSA on metal substrates. The alternating stress evolution for Ni-free Cu-deposition (black curve) from compressive to tensile and again towards a compressive state is well known for high surface mobility films that grow by a Volmer-Weber mechanism [8]:

During the early stages of nucleation, before the film has coalesced, the film stress is compressive. This has been attributed to the effect of surface capillary forces on the isolated clusters. At the point of island coalescence, a tensile stress develops which is associated with the formation of grain boundaries. After further growth to form a fully continuous film, the tensile stress is observed to decrease again. In the presence of the growth flux, the chemical potential of the surface is higher than it would be if the surface were in equilibrium. Raising the chemical potential on the surface provides a driving force that causes the flow of atoms into the grain boundary. The incorporation of excess atoms into the grain boundary creates a compressive stress in the film. Theoretically this stress contribution should be reversible and indeed, if the deposition is interrupted, we observe a rapid relaxation towards tensile stress for the black curve in Fig.4 (not shown here). In this stage of growth the total film stress can be estimated [8]:

$$\sigma = \sigma_i - \sigma_0 \cdot N_{gb}\left(\frac{a}{h}\right) \tag{3}$$

Here “a” is the atomic spacing, h is the height of a grain, N_{gb} is the flow of atoms into the boundaries and σ_i is a tensile stress that develops as the planes in adjacent clusters grow together to form a grain boundary. This tensile component is assumed as being constant due to the cohesive attraction between atoms at the boundary of grains. σ_0 corresponds to the compressive stress that would result if an additional atom were added to each of the atomic planes in the grain boundary.

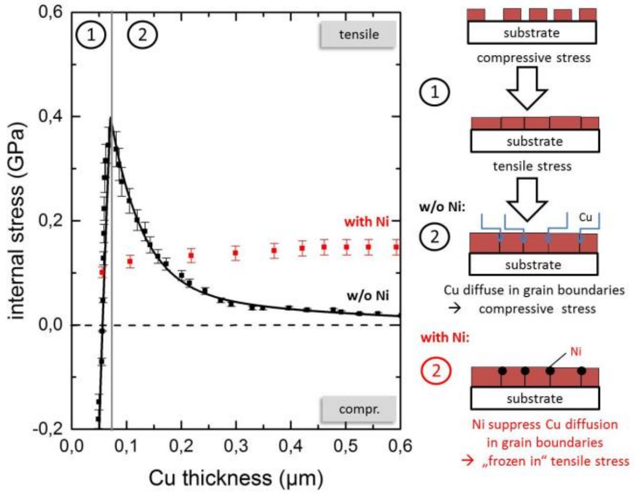

Fig.4) a) In-situ internal stress as a function of deposited Cu thickness for a Ni-free electroless bath (black curve) and for an electrolyte with Ni-conc. of 400ppm (red curve). Stress evolution is explained by coalescence of Cu-clusters and Cu-atom diffusion in grain boundaries (details see text)

σ_0 contains the elastic modulus and a shape factor and is proportional to the grain boundary density. By means of (3) the stress behavior from Ni containing bath (red curve in Fig.4) can be interpreted in terms of a low surface mobility of Cu-atoms. In this case, Cu-atoms are kinetically limited from being incorporated into the grain boundary so that N_{gb} =0 in (3), results in a widely constant tensile stress state. Furthermore the reduction of Cu-diffusion length by co-deposited Ni explains the generally finer grain structure, observed for Ni-containing electroless copper baths (see Fig.2).

C. Impact of NaOH

To test the influence of NaOH we use a tartrate based electroless copper bath with a cyanide free nitrogen-sulphur stabilizer system at a bath temperature of 34°C without induced liquid flow and a constant Ni-concentration of 140ppm. NaOH-conc. of the bath was varied from 4g/l to 20 g/l. The internal stress was measured by in-situ DSA on

ABS-substrates (see Fig.5). An increase of NaOH-conc. reduces the tensile stress from 0.6 GPa (4g/l NaOH) to about 0.2 GPa (12g/l NaOH) by affecting the incorporated Ni in the electroless Cu film (-30%). For film thicknesses above 0.1µm the curves show a roughly constant tensile stress during Cu growth, an indication of permanently suppressed Cu mobility in grain boundaries. This holds also for baths with high NaOH conc., and it seems that, especially in this case, the relative small amount of incorporated Ni prevents Cu-diffusion into grain boundaries (N_{gb}=0 in (3)). The lower tensile stress for increased NaOH-conc. is probably caused by influencing the Cu-growth in the first stage of growth (nucleation and coalescence), whereas e.g. a lower Ni-codeposition can modify the Cu-grain size.

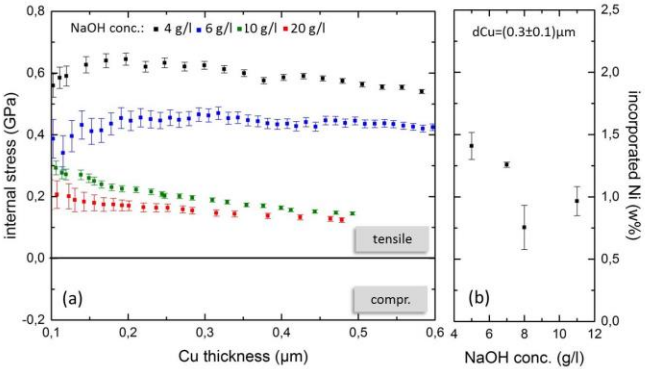

Fig.5) a) internal stress, measured by in-situ DSA on ABS-substrate, as function of deposited Cu-thickness for different NaOH-conc. in electroless copper bath (140ppm Ni) b) incorporated Ni in a 0.3µm thick Cu-layer on ABS-substrate as function of NaOH-conc.

Nevertheless NaOH-conc. in electroless Cu electrolytes is a main impact factor for internal stress that affects substantially the Ni-incorporation in the deposit.

C. Impact of Cyanide concentration and Substrate

To test the influence of cyanide we prepare a tartrate based electroless Cu bath with a cyanide stabilizer system and a NaOH-conc. of 9 g/l at a bath temperature of 34°C without explicit liquid flow and a constant Ni-concentration of 400 ppm. The cyanide-component in the stabilizer system was varied from 0ppm to 72ppm. The stress measurements were carried out with metal substrates (Fig.6).

Increase of cyanide from 0ppm to 36ppm lead to a 50% decrease of codeposited Ni (from 2.4w% to 1.2w%), accompanied by a gradual reduction of internal stress from 50 MPa (0 ppm CN^-) tensile to 0.0 MPa (20 ppm CN^-) for a 0.3µm thick electroless Cu film. In that case the internal stress tends to an asymptotic decrease as function of deposited thickness and reaches the compressive state for cyanide concentrations >36ppm and at a thickness of about 0.4µm. This indicates insufficient suppression of Cu-diffusion (N_{gb} >0 in (3)) by incorporated Ni. This is surprising due to a still high incorporated Ni-content of more than 1w% (Fig.6b). For NaOH variation (Fig.5) a similar codeposited Ni-content of 0.75-1.0w% (corresponds to >10g/l NaOH) leads to a constant level of tensile stress. The fact that the same amount of incorporated Ni can suppress Cu-diffusion in grain boundaries (in case of NaOH-variation) or not (in case of CN^-variation) points to a reduced efficiency of incorporated Ni in the second case, e.g. by a different kind of Ni-incorporation or Ni-passivation.

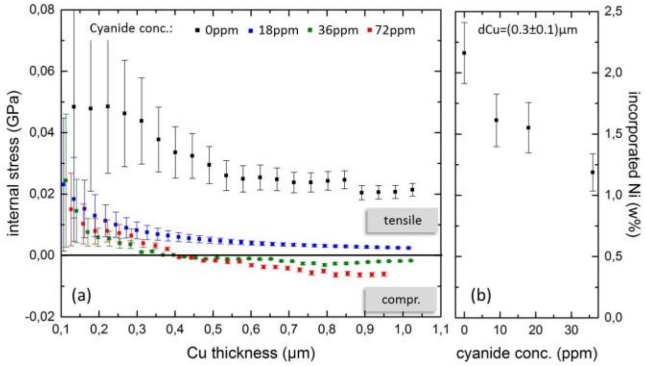

Fig.6) a) internal stress, measured by in-situ DSA on metal-substrate, as function of deposited Cu-thickness for different cyanide-conc. in electroless copper bath (400ppm Ni) b) incorporated Ni in a 0.3µm thick Cu-layer on FR4-substrate as function of Cyanide-conc.

For higher cyanide contents blister generation is observable, in accordance to the concept of critical compressive stress (1).

However a direct comparison of absolute stress values of Fig.5) and Fig.6) is invalid, due to a different kind of used substrates. Nevertheless experience has shown that DSA measurements on metal substrates (Fig.6) show generally about 35% lower stress values compared to ABS-substrates under identical electroless bath conditions. From Section II b) it is evident that the total internal stress of thin films (<3µm) critically depends on the nucleation density, size, density and shape of Cu-grains. In the initial stage of growth these parameters were predefined from the substrate surface. Desmeared ABS-substrates have a rough and micro-porous surface compared to the smooth surface of a metal substrate. Aside from different stresses induced from ABS and metal substrates to the copper layer, the roughness of the substrate surfaces plays a decisive role. Tests with ABS-substrates by variations of roughness, shows significant different stress slopes in the initial growing phase (<0.1µm).

In summary, cyanide modifies substantially the internal stress of electroless Cu and the codeposition of Ni. There are indications that cyanide reduces the function of incorporated Ni to trap diffusive Cu adatoms.

D. Impact of liquid flow

Fig.7b) illustrates the incorporated fraction of Ni as a function of Cu thickness, with and without flow. Here we used a cyanide free, tartrate based bath (T = 32 °C) with a Ni-conc. of 400 ppm. Liquid flow was generated by a moderate automated sample movement in the Cu bath.

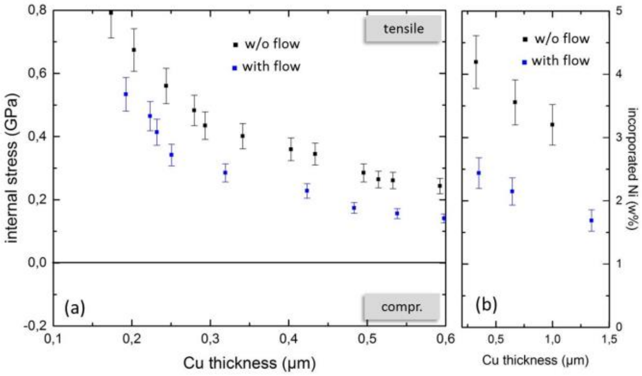

Fig.7) a) residual internal stress, measured ex-situ by DSA on metal-substrate, as a function of deposited Cu-thickness under different bath-flow conditions b) incorporated Ni as function of Cu-thickness on FR4-substrate with and without (w/o) bath- flow

A remarkable impact of bath flow on Ni codeposition can be deduced. In fact, the incorporated Ni fraction in Cu layer without any liquid flow is twice as high as under flow conditions over the whole range of Cu-thickness. Without flow, the reduced liquid exchange at the liquid-solid interface leads to a depletion of Cu-concentration. As a result of an increased Ni/Cu-ratio a higher Ni fraction is co-deposited. This probable scenario explains also the decrease of incorporated Ni by continued Cu growth. In the initial growth phase the roughness and micro-porosity of the substrate enables microscopically regions without any Cu-mass exchange, e.g. in µ-caverns. Here Cu-content depletes and a relatively high amount of Ni can be deposited. During plating, the surface is leveling out, accompanied by a more efficient copper mass exchange at the liquid-solid-interface. In consequence, the co-deposited Ni fraction decreases. In accordance to this we found significantly more incorporated Ni in Cu films on rougher substrates (e.g. FR4 vs. ABS). It is evident that on structured PCB-substrates, e.g. in the case of blind micro vias (BMV) or VIA^2-technology, this effect can play a decisive role and substantially higher fractions of Ni can be deposited within these structures. Again this can potentially affect subsequent process steps, e.g. BMV-filling etc.

DSA is unable to measure the in-situ stress with liquid flow, due to the flow induced movement of test strips. Thus, we measure here the *residual stress* after plating at different copper thicknesses. Since the relaxation of internal stress sets in, instantaneously after deposition, this will affect the ex-situ DSA measurement. Therefore, a direct interpretation in the framework of Cu-mobility is not applicable. Nevertheless also the residual stress correlates to the fraction of codeposited Ni (Fig.7). The copper layer deposited without bath flow indicates remarkably higher residual stress values as those plated under flow conditions. A clear indication that liquid flow is a further main impact factor for internal film stress.

E. Impact of bath aging and other components

The following table summarizes typical by-products and components in electroless baths without impact on internal stress, here measured by in-situ DSA:

Table 1)

material	tested range
Methanol	0 - 50 ml/l
Sodium Sulphate	0 - 50 g/l
Sodium Formate	0 - 50 g/l
Formaldehyde	8 - 64 ml/l

III. Conclusion

Increase of Ni-concentration in electroless Cu electrolytes intensifies the Ni-codeposition. The incorporated Ni^0 (up to 4.2 w%) reduces Cu diffusion at grain boundaries and preserves the previously attained tensile stress state. The comparison of In-situ DSA measurements in electroless Cu baths with and without Ni confirms this proposal. Aside from Ni-concentration, we identified further bath components and bath conditions which modify substantially the Ni-incorporation and the internal film stress as well. An increase of NaOH from 4g/l to 20 g/l reduces the incorporated Ni by 30%, accompanied by a tensile stress reduction of about 60%. Increase of cyanide (as a widely used stabilizer component) from 0 to 36 ppm leads to a 50%

reduction of incorporated Ni, combined with a 100% loss of tensile stress, a turn towards compressive behavior and a higher risk of blistering. Also bath flow plays a decisive role in Ni-codeposition, whereas higher flow reduces Ni-incorporation by about 50% together with decrease of residual tensile stress of about 25%. In this context the surface roughness of PCB-substrates modifies the Ni-codeposition and leads to a linear depth profile of incorporated Ni.

Understanding this interplay opens the potential to optimize the internal film stress by use of other or alternative electrolyte components.

References

[1] R. Huemoeller, S. Rusli, S. Chiang, T.Y. Chen, D. Baron, L. Brandt and B. Roelfs, Advancing Microelectronics, 34, 22 (2007).

[2] P. Hutapea and J. L. Grenestedt, J. Electron. Packaging, 126, 82(2004)

[3] Tobias Bernhard et. al "Analysis of stress/strain in electroless Cu films",46th International Symposium of Microelectronics, Orlando, (2013).

[4] Tobias Bernhard, Frank Bruening, Ralf Bruening, Tanu Sharma, Delilah Brown, Sebastian Zarwell, Craig Bishop, JMEP, 12, 86-91 (2015)

[5] Ralf Bruenning, will be published

[6] Simon Bamberg et. al, Thin Solid Films, Volume 520, Issue 23, Pages 6935-6941 (2012)

[7] Ralf Brüning et. al, Thin Solid Films, Volume 565, Pages 136-142 (2014)

[8] E. Chason, B.W. Sheldon, L. B. Freund, J. A. Floro and S. J. Hearne, Phys. Rev. Lett. Vol.88, No. 15 (2002)