The use of Ultrasound to Enable Low Temperature Electroless Plating

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IMFair

RAF Museum Cosford, UK

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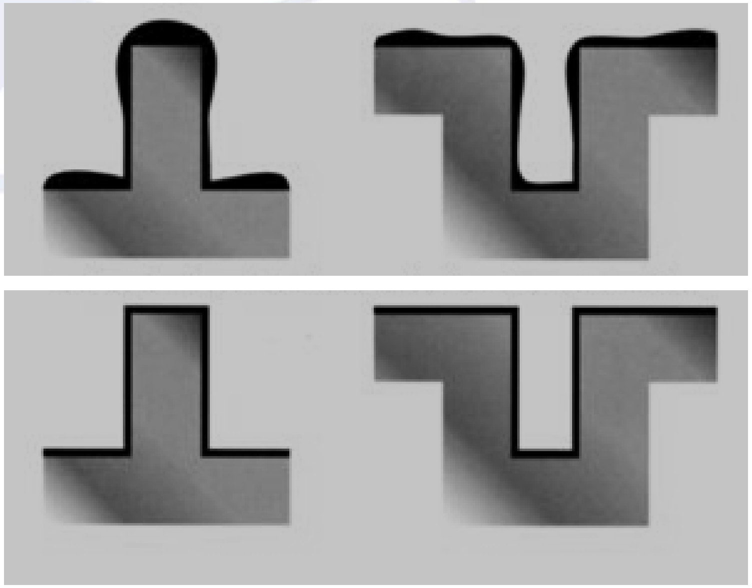
Agenda

1. The properties and applications of electroless nickel plating in manufacturing
2. Sonochemistry
3. Previous work on the effect of ultrasound on electroless plating
4. The use of ultrasound for low temperature electroless nickel plating
   - Experimental approaches
   - Results
   - Conclusions

The Properties of Electroless Nickel

Corrosion protection
Hardness and wear resistance
Uniform coating thickness
Anti-friction
Metals, plastics, composites can be plated
Composite coatings can be deposited e.g. PTFE



Electroplated Thickness Distribution

Electroless Thickness Distribution

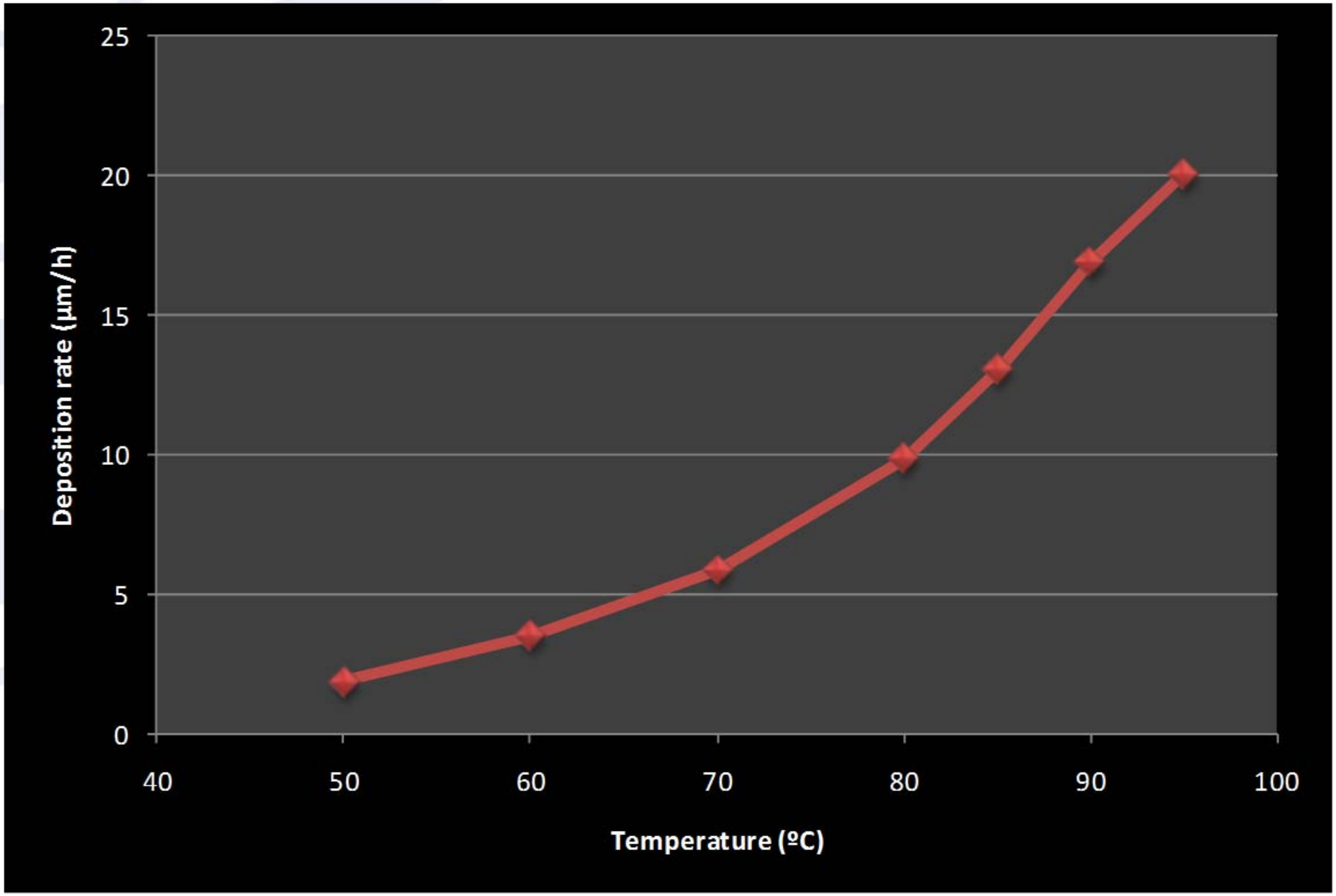
Applications of Electroless Nickel

Electroless Nickel can be deposited on a wide range of substrates and has found a number of applications in the Aerospace industry

Aircraft Engine Parts
Valves
Pumps
Hydraulic Pistons
Splines
Gears
Housings
Turbine Components
Electronic Components (solderable finish)

Effect of Temperature on Electroless Nickel

The main effect on electroless nickel plating rates is temperature



After Reidel W., 1991, Electroless Nickel Plating, Finishing Publications Ltd, Stevenage, England

Problems with high temperature Electroless Nickel

To obtain electroless nickel thicknesses required for many manufacturing processes within a reasonable time scale most electroless nickel processes are operated in excess of 80 ºC

The consequences High temperature operation

- **High energy costs**
- **High water usage (due to evaporation)**
- **Bath instability**
- **Health and safety – fume/mist from above tank**

Can plating temperatures be reduced without plating rates or quality of deposit dropping?

Aims and Objectives of the UlteiMet project

Three Year project funded by the IeMRC (Innovation in electronic manufacturing Research Centre)

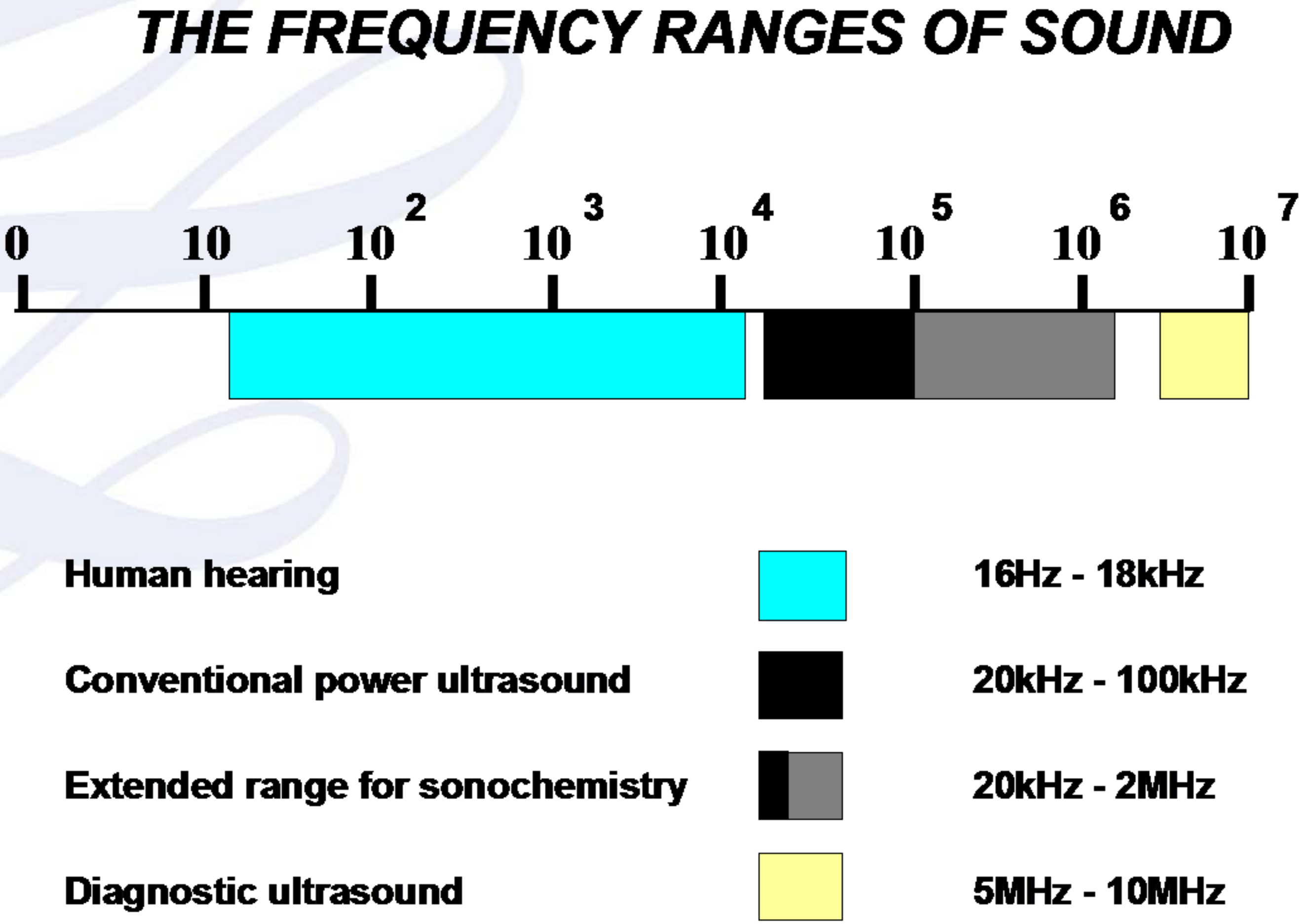
The ULTEIMet project

Ultrasonically enabled Low Temperature Electroless and Immersion Metallization

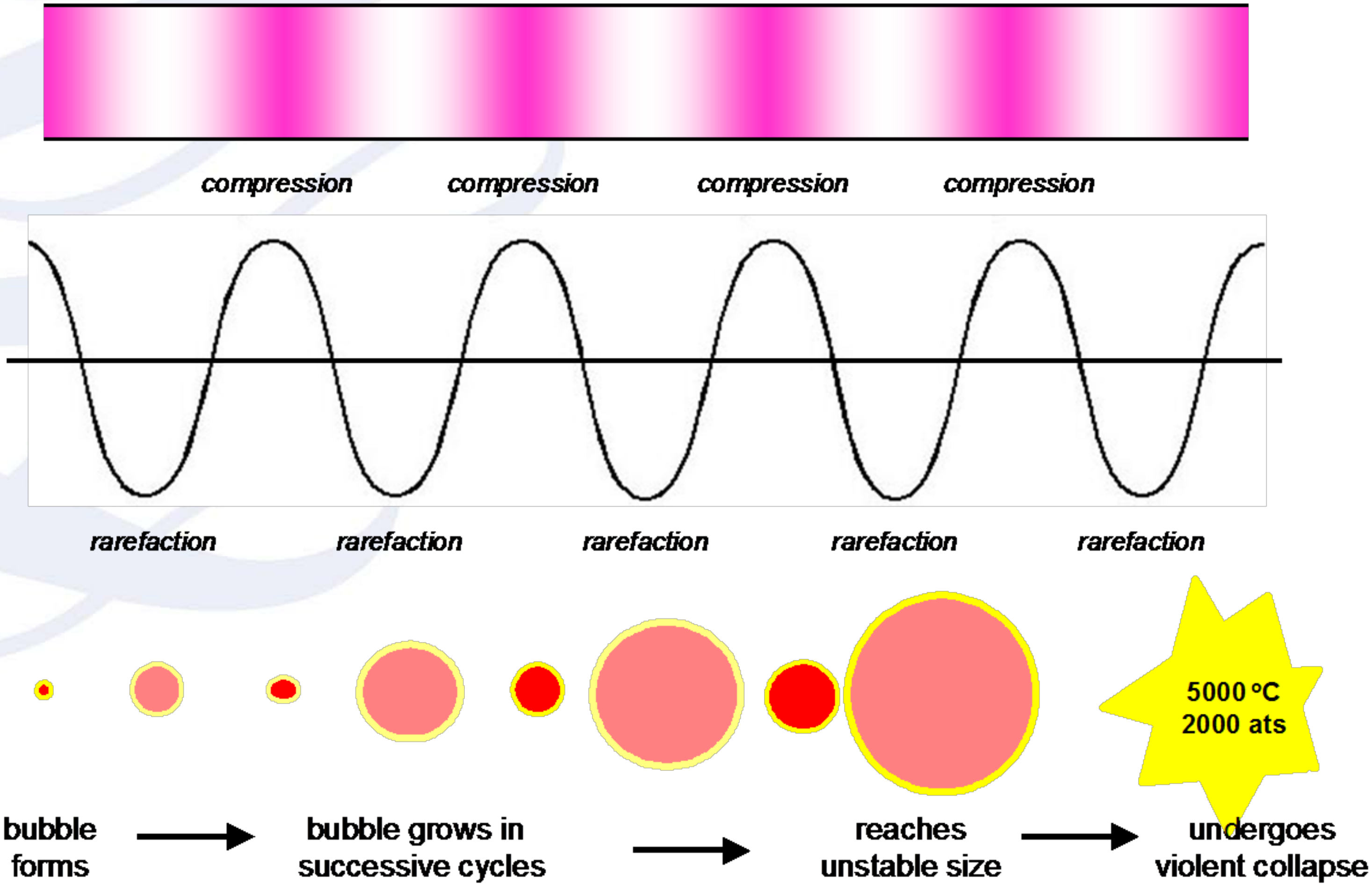
Project Objective – "Reduce the temperatures used in electroless and immersion plating processes by the application of ultrasound"

Sonochemistry

The effect of sound on the chemistry of a solution

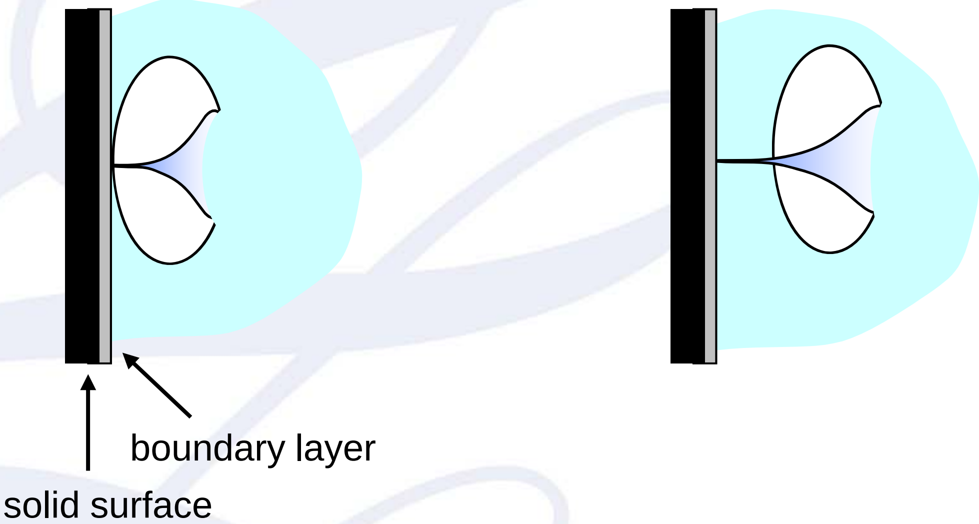


Acoustic Cavitation

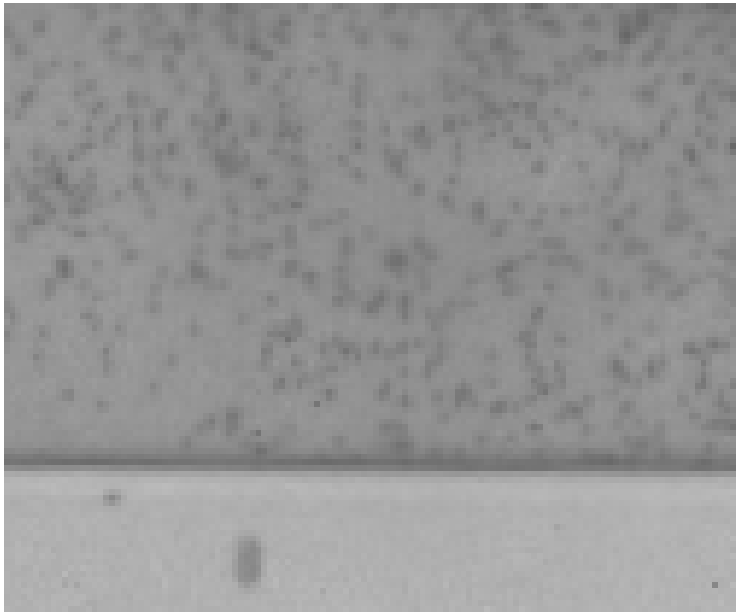


Microjetting/Microstreaming

Acoustic Cavitation in a liquid ***NEAR A SURFACE***



UNSYMMETRIC COLLAPSE
Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface



Video courtesy of University of Twente, Netherlands. and Shimadzu Europa GmbH, Duisburg, Germany

Electrochemical Effects

Thinning of diffusion layer
Improved mass transport
Improved solution movement
Electrode cleaning
Degassing etc

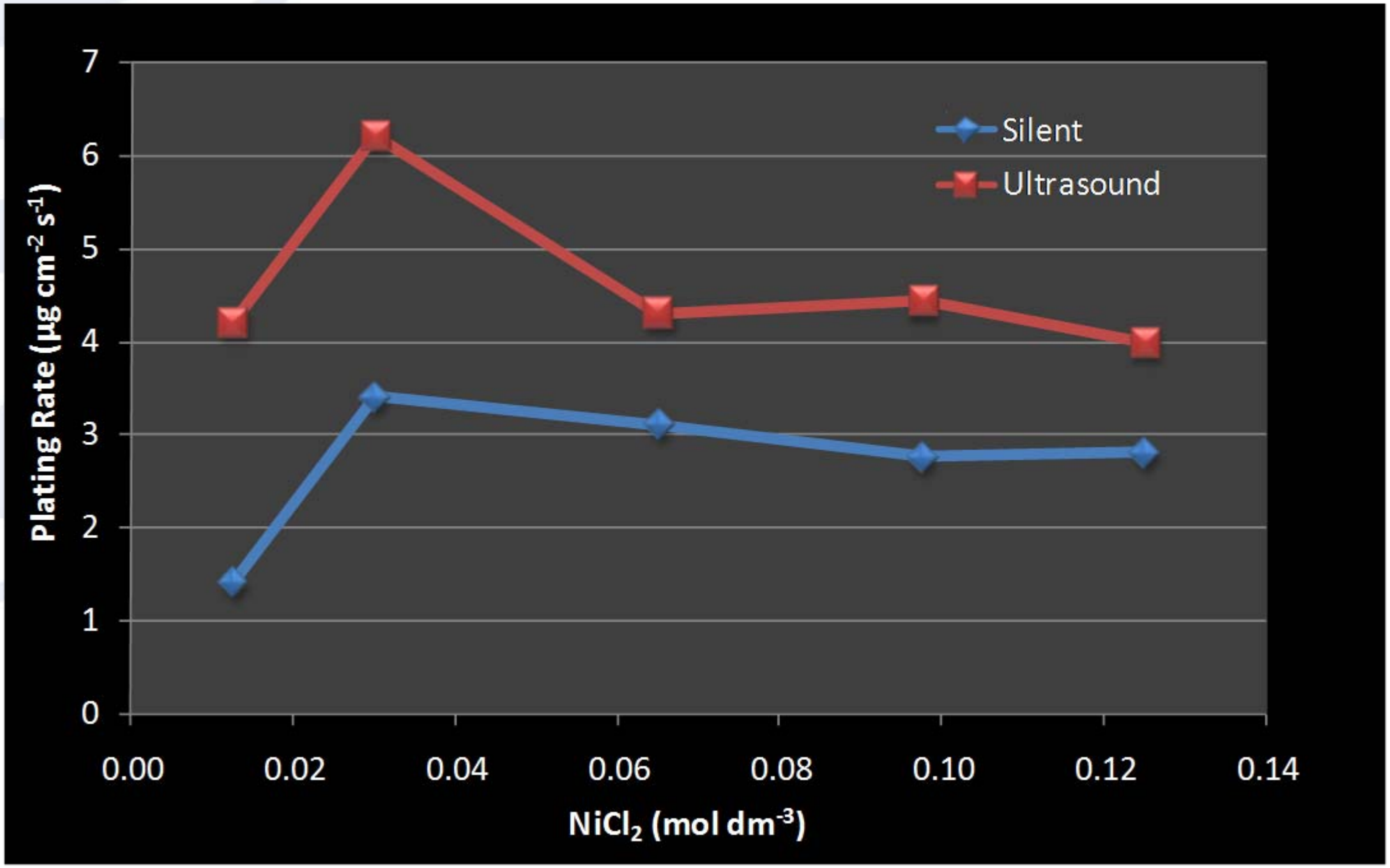
ELECTROLESS PLATING IN AN ULTRASONIC FIELD
Effect Of Ultrasound on Plating rate

Workers	Plated Metal	Reducing Agent	Effect of Ultrasound on Plating Rate	
			Increase	Decrease
Abyaneh et al	Nickel	Hypophosphite	Yes – low complexing agent – no additives	Yes – high complexing agent , added thiouera
Chiba et al	Nickel	DMAB	Yes	
Mallory	Nickel	Hypophosphite	Yes – low thiourea concentrations	Yes – High thiourea concentrations
Matsuoka and Hayashi	Nickel	Hypophosphite	Yes – but less if use strong complexing agent	
Yang et al	Nickel	Hypophosphite	Yes	
Touyeras et al	Copper	Formaldehyde	Yes	
Zhao et al	Copper	Formaldehyde	Yes	

ELECTROLESS NICKEL PLATING IN AN ULTRASONIC FIELD

Ultrasonic frequency – 38 kHz, Bath Temperature 90 ºC, No additives, pH 4-5

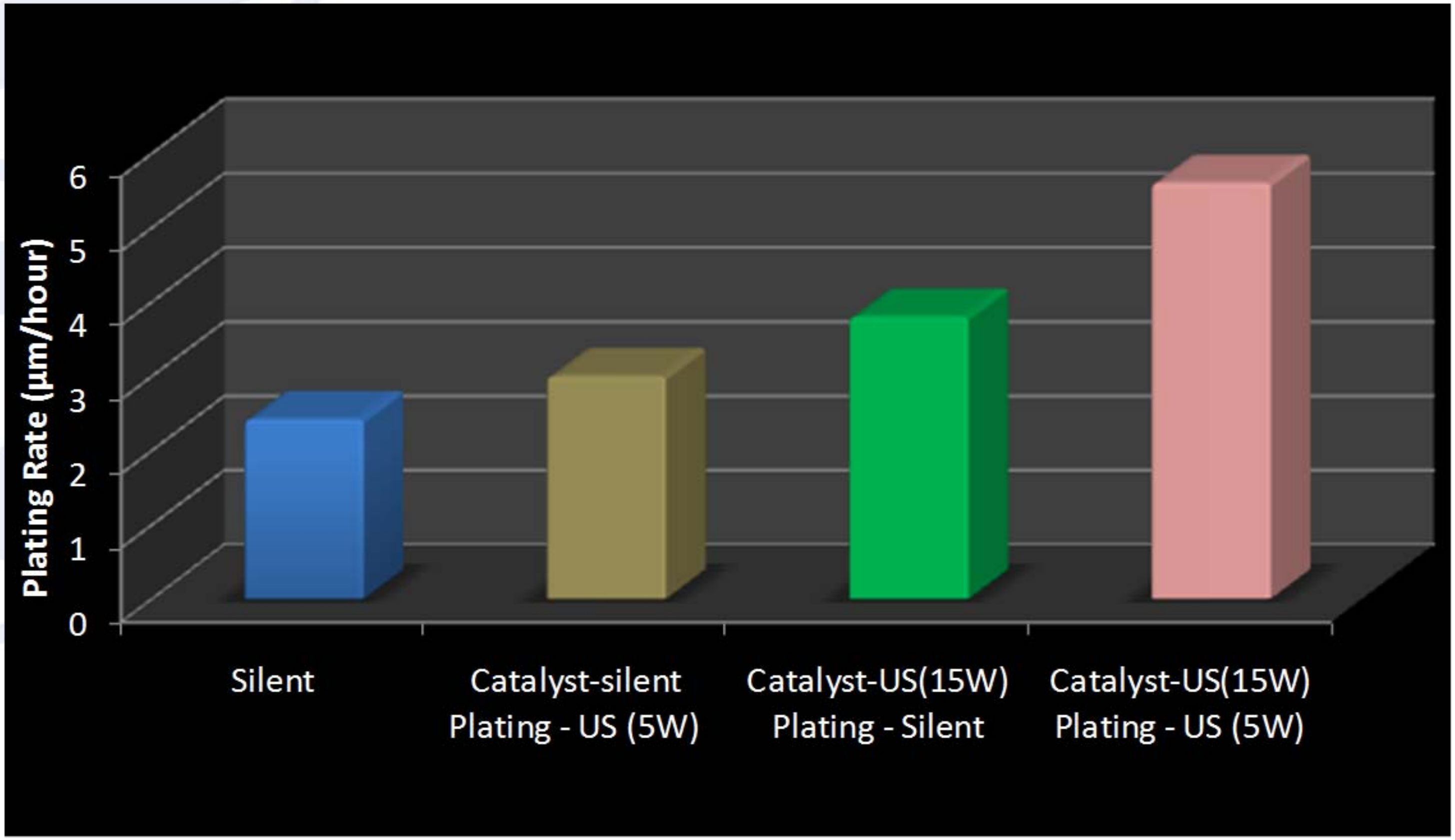
Low Sodium Acetate Conc (0.04 mol/dm^{-3})



M.Y.Abyaneh, A.Sterritt, T.J.Mason
J.Electrochem.Soc., 154 (9) D467-D472 (2007)

ELECTROLESS COPPER PLATING IN AN ULTRASONIC FIELD

Ultrasonic frequency – 530 kHz



Data reproduced by kind permission of;

F. Touyeras et al

Ultrasonics Sonochemistry 10 (2003) 363–368

Effect of Ultrasound on Electroless plating

Theories for increased in plating rate:

- Improved mass transport
- Thinning of Diffusion layer
- Crystal structure formed under ultrasonic conditions in initial stages of plating(Abyaneh et al)
- Activation of hypophosphite (Mallory)
- Localized heating in diffusion layer (Touyeras et al)
- Activation of Catalyst (Touyeras et al)
- Degassing

All previous work carried out at normal operating temperature

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating Feasibility work

Two approaches

1. **Electrochemical study**
   -mixed potential theory

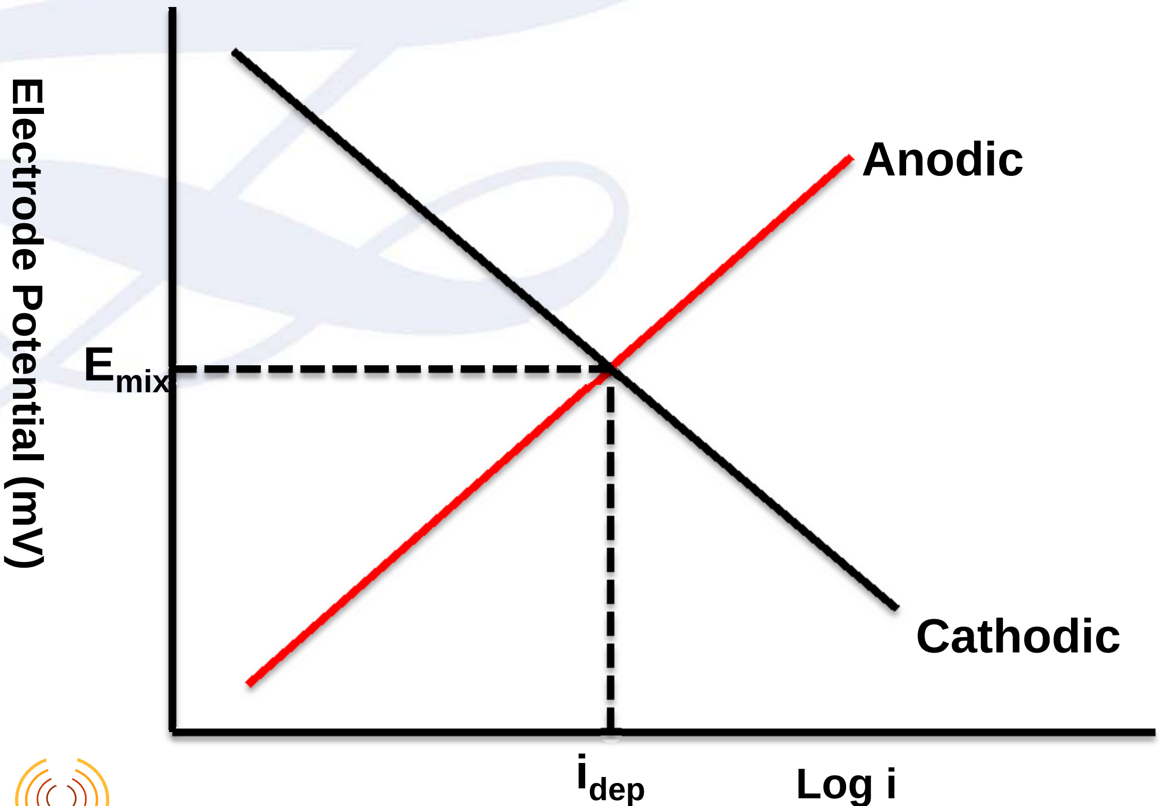
2. **'Applied' study**
   -test coupons plated in electroless nickel solution

Electroless Nickel Formulation

Constituent	
$NiCl_2$	30 g/l
NaH_2PO_2	40 g/l
Sodium Citrate	25 g/l
Ammonium Chloride	40 g/l
Temperature	50, 70, 90 ºC
pH	5.2

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating
Mixed Potential Theory

In electroless plating the anodic and cathodic reaction occurs on the same substrate. Therefore there must be common potential at which both reactions occur (the mixed potential). The current density at this point should be related to the deposition rate.



Determine cathodic polarization curve on electroless solution without hypophosphite.

Determine the anodic polarization curve in electroless solution without nickel salt.

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating
Plating Tests

Copper clad 2.5 cm X 2.5 cm epoxy test coupons
Plating rate determined using weight gain
Plating time – 1 hour

Other factors determined
- **Phosphorus content in deposit (ICP)**
- **Brightness (Glossmeter)**
- **Microhardness (Vickers)**

In mixed potential study and 'plating tests' ultrasound was applied using a 20 kHz ultrasonic probe with a power density of 42 W/cm^2

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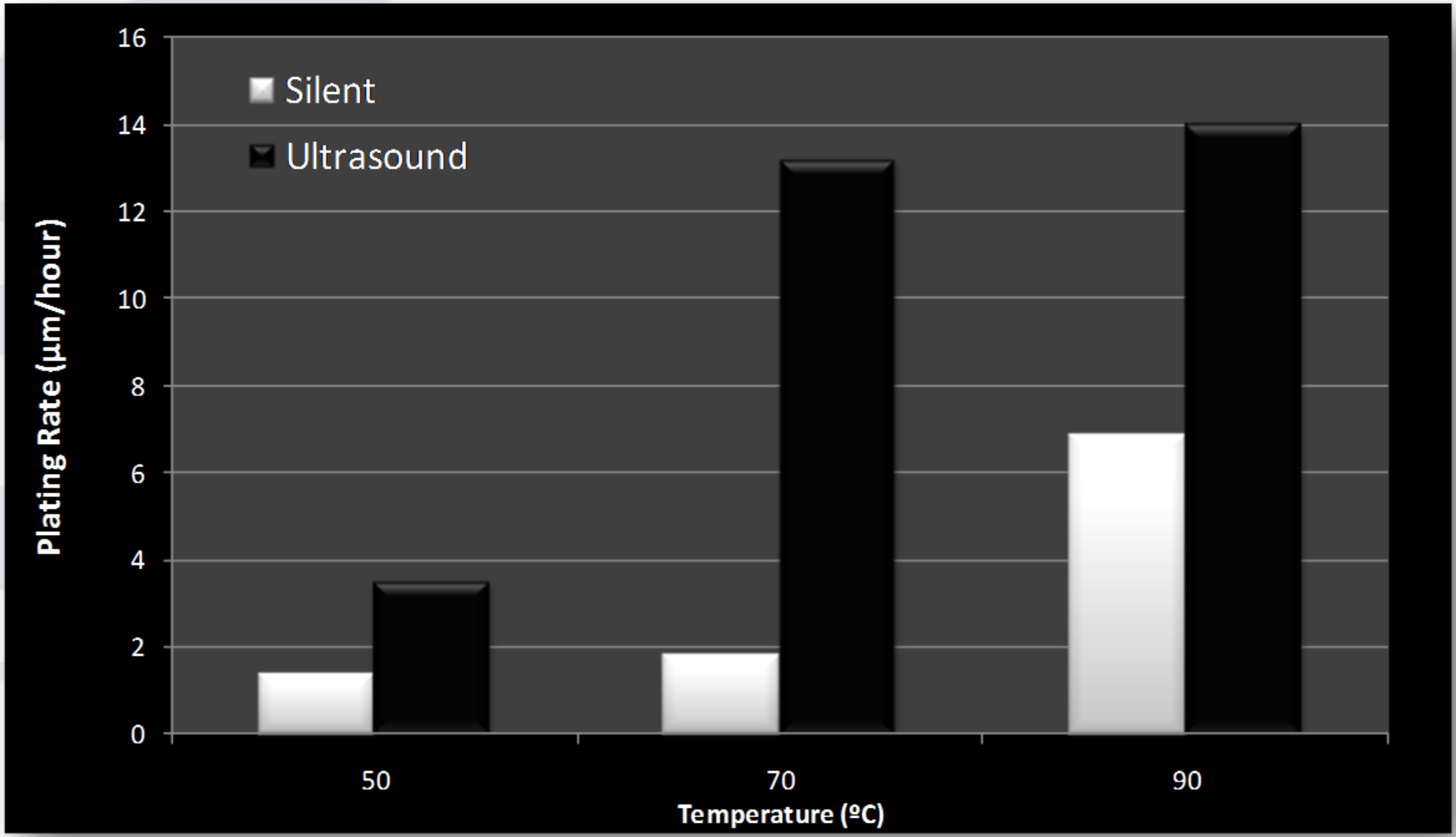
Plating rate determined using Mixed Potential theory



Plating rate with ultrasound always higher

Plating rate at 70 ºC with ultrasound 2 X higher than 'silent' plating rate at 90 ºC

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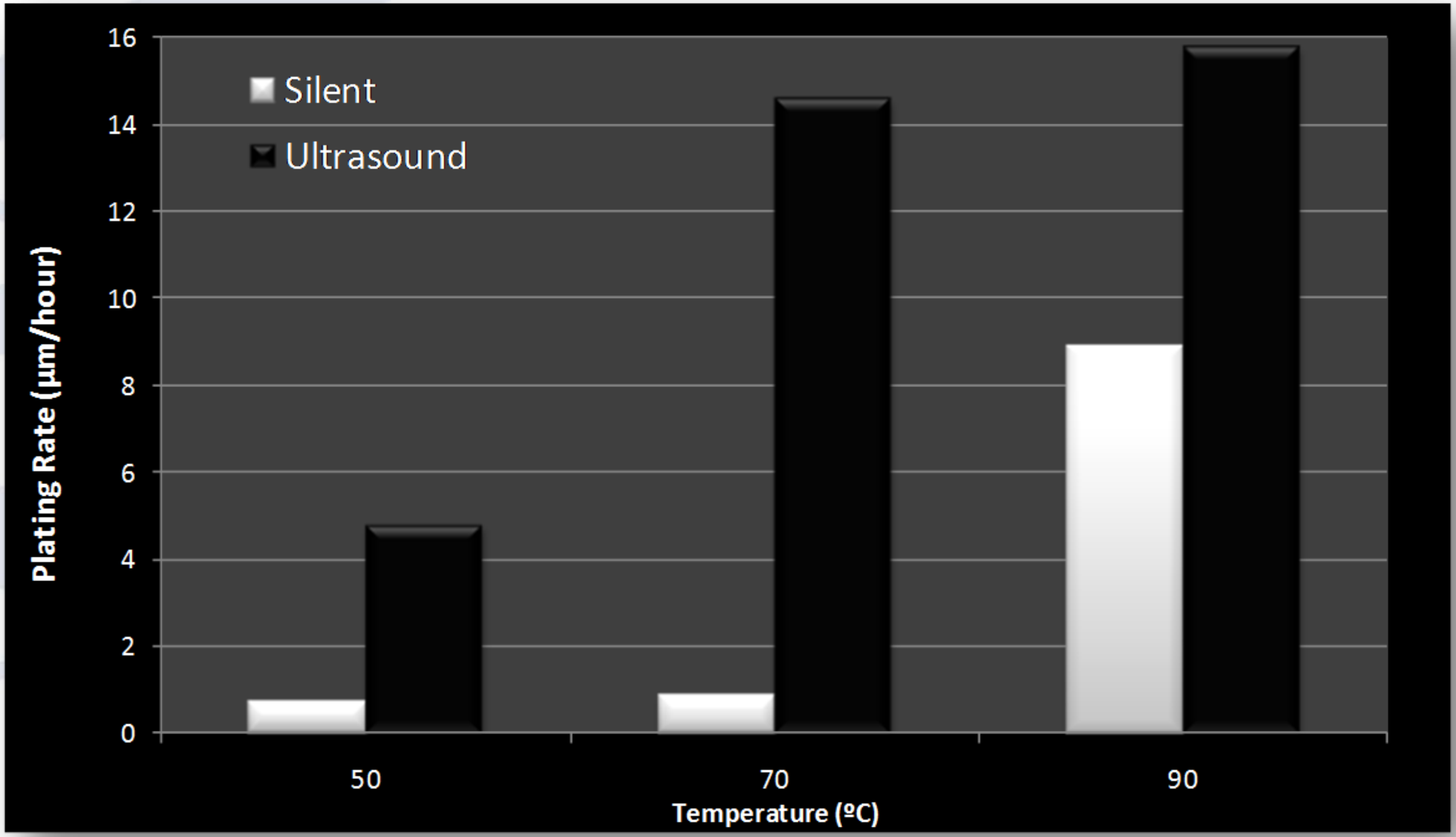
Plating rate determined using Weight Gain



- **Plating rate with ultrasound always higher**
- **Plating rate at 70 ºC with ultrasound 1.5 X higher than 'silent' plating rate at 90 ºC**
- **Good agreement between two approaches for measuring plating rate**

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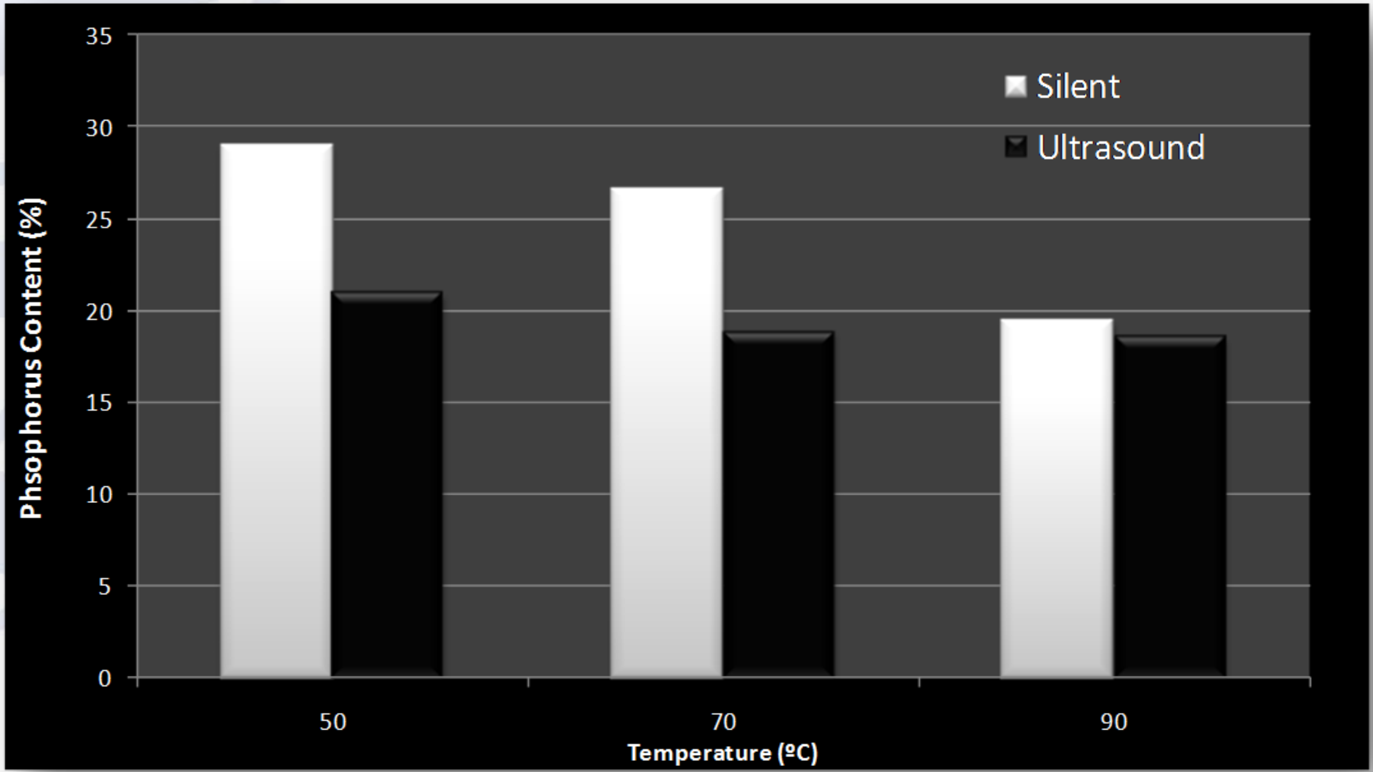
Effect of Ultrasound on Phosphorus content in Deposit



Phosphorus content generally lower with ultrasound

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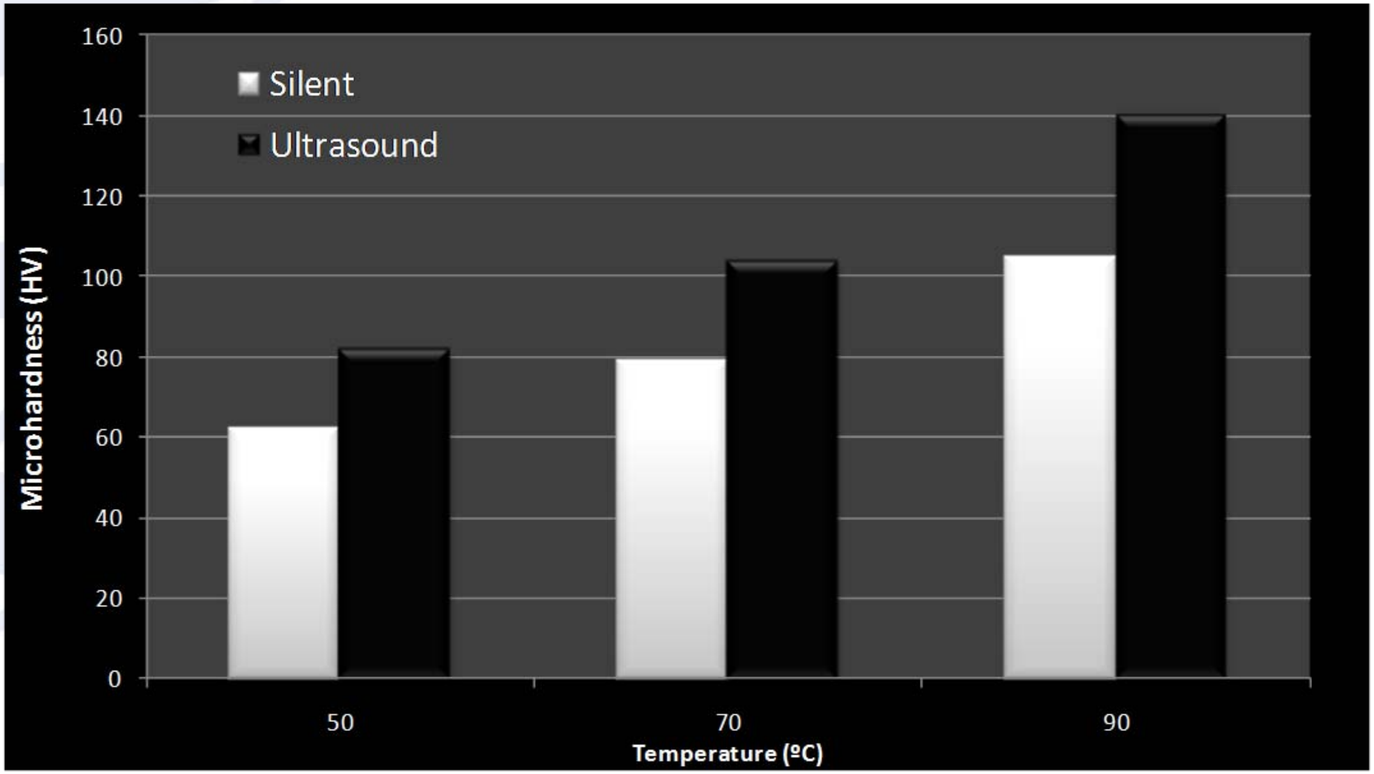
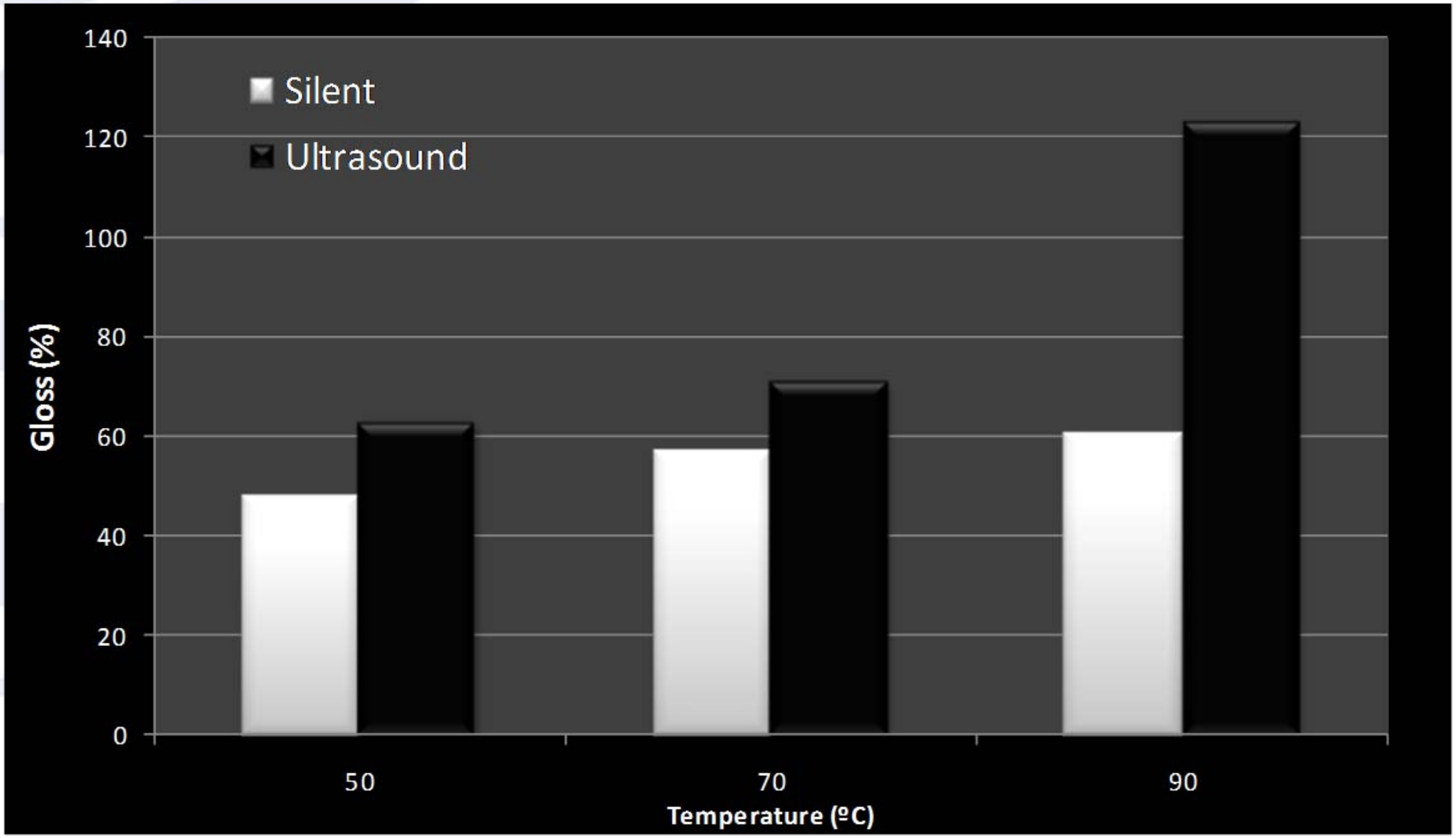
Effect of Ultrasound on Microhardness of Deposit



Microhardness higher when use ultrasound
Related to lower phosphorus content in deposit
Change in crystal structure of deposit in an ultrasonic field

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating

Effect of Ultrasound on Brightness of Deposit (Gloss)



- Brighter deposit produced in an ultrasonic field.
- Change in deposit structure
- Finer grained deposit produced using ultrasound

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating
CONCLUSIONS

1. **Very promising results from this initial study**
2. **Ultrasound always produced higher plating rates using the electrochemical approach or ‘weight gain’**
3. **Plating rates at 70 ºC in an ultrasound field were 1.5-2.0 X higher than those obtained under ‘silent’ conditions.**
4. **Good agreement between plating rates using the 2 techniques**
5. **Phosphorus content always lower when plating performed in an ultrasonic field**
6. **Microhardness higher on deposits plated using ultrasound**
7. **Brightness (gloss) higher when plate in an ultrasonic field**
8. **From ‘6’ and ‘7’ strongly suggests deposit structure is changed when plating in an ultrasonic field.**

The use of Ultrasound to Enable Low Temperature Electroless Nickel Plating

Project funded by

IeMRC Innovative electronics Manufacturing Research Centre

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Thank you

Any Questions ?