Innovation and Application of Nanoscience Thematic Program

Synthesis of Polymer-Capped Pd Nanoclusters and Its Application in Next Generation Microelectronic Manufacturer(I)

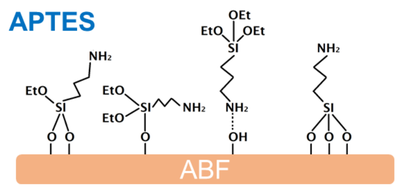
Vidya Kattoor, Yi-Cang Wu, Pei-Qing Yang, Pei-Tsen Wei, Tzu-Chien Wei*

Department of Chemical Engineering National Tsing-Hua University 300 Hsinchu, Taiwan (R.O.C)

NSTC: 111-2124-M007-006

Introduction & Aims

- **Novel Self-adsorption Catalyst Application Metallization Process :**
  1. Silane Compound Coating for Self-Adsorption of Nano-Pd and ABF High-Adhesion Wet Metallization Process
  2. Blending PEI with PVA-Pd as Self-Adsorbing Catalyst on Electroless Copper Plating (ELP)
- **Application of 5G Generation Nano Pd Metallization :**
  1. Ultra Thin Peelable Copper Foil Technology
  2. Via Micro-Roughening (MR) Treatment and Polymer-Capped Pd Catalyst to Achieve High Adhesion Metallization Manufacturing



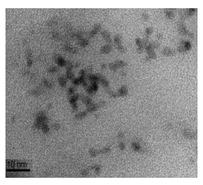
Novel Self-Adsorption Catalyst Application Metallization Process

Methods

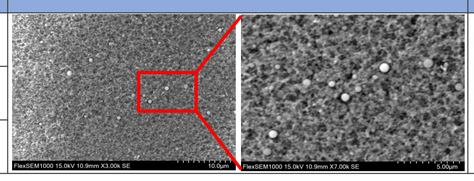
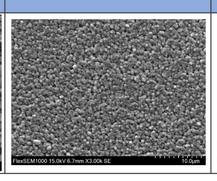
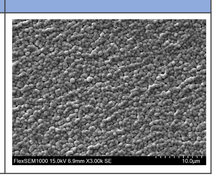
Sn/Pd (Commercial Process)	Sn/Pd RT 10 min → Water wash RT 1 min → HCl RT 5 min → Water wash RT 1 min → Cu ELP 36 ºC 15 min
1-Step APTES-Pd (EELab Process)	Activation RT 10 min → Water wash RT 1 min → Cu ELP 36 ºC 15 min → Cu / APTES-Pd / ABF
1-Step PEI+PVA-Pd (EELab Process)	Activation RT 10 min → Water wash RT 1 min → Cu ELP 36 ºC 15 min → Cu / PEI and PVA-Pd hybrid layer / LCP

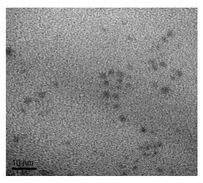
*ABF substrate is from Unimicron

Results & Data Analysis

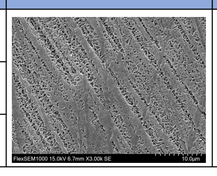
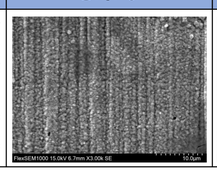
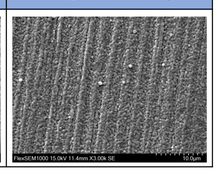


TEM image of APTES-Pd

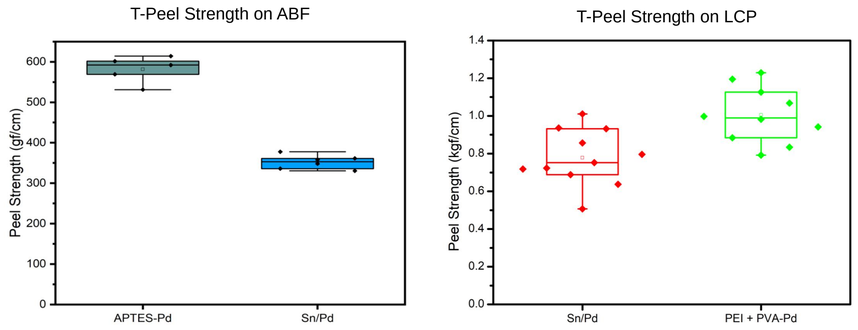
ABF Roughness (μm)		ABF bare	Copper Deposit for 15 min ELP	
			Sn/Pd	APTES-Pd
Ra	0.026±0.004			
Rq	0.034±0.006			
Rz	0.167±0.030			



TEM image of PEI+PVA-Pd

LCP Roughness (μm)		LCP bare	Copper Deposit for 15 min ELP	
			Sn/Pd	PEI + PVA-Pd
Ra	0.131±0.027			
Rq	0.163±0.035			
Rz	0.656±0.144			

✓ Adhesion Performance: T-Peeling



✓ Quantitative Analysis: Catalyst Activity Performance

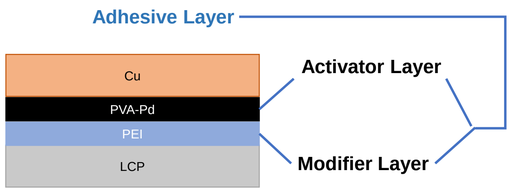
Cu/Pd Ratio Rate (for 5 min ELP):	Commercial Catalyst Sn/Pd	1-step Catalyst PEI + PVA-Pd
Working concentration (ppm)	250	50
Pd adsorption capacity (μg/dm²)	93.472	14.340
Cu loading (μg/dm²)	7526.111	5950.690
LCP Cu/Pd ratio	**80.517**	**414.964**

Conclusions

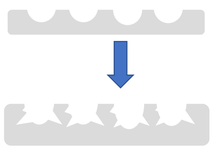
1. **Silane Compound Coating for Self-Adsorption of Nano-Pd and ABF High-Adhesion Wet Metallization Process:**
   - Successfully synthesized the self-adsorption catalyst APTES-Pd, in which the process is easier and faster than Sn/Pd.
   - The average peel strength when using APTES-Pd as catalyst is 582 gf/cm, which is better than 352 gf/cm when using commercial catalyst.
2. **Blending PEI with PVA-Pd as Self-Adsorbing Catalyst on Electroless Copper Plating (ELP):**
   - Successfully used PEI + PVA-Pd as an activator to ELP copper on LCP.
   - The average Cu/Pd ratio of 1-step PEI + PVA-Pd catalyst is 5.15 times better than that of commercial catalyst on LCP.
   - The average peel strength when using PEI + PVA-Pd as catalyst is 1.005 kgf/cm, which is better than 0.778 kgf/cm when using commercial catalyst.

Application of 5G Generation Nano Pd Metallization

Methods

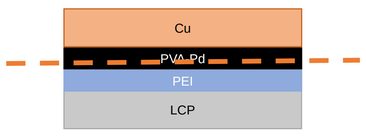


Micro-Roughening (MR)

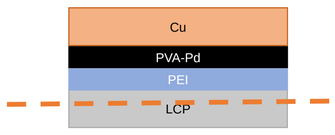


Desmear + Neutralizer

◆ Peelable Copper Foil Technology



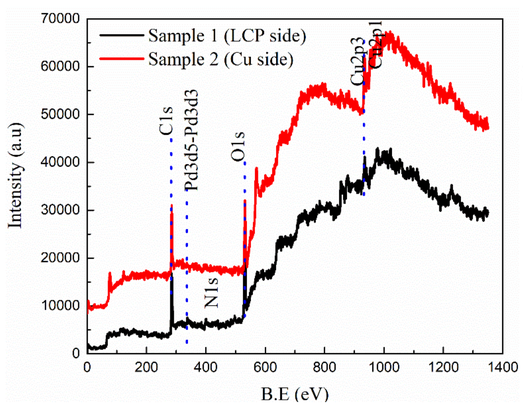
◆ High Adhesion Copper Foil Technology

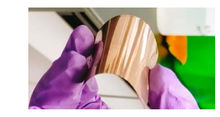


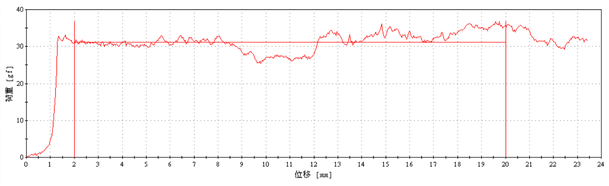
Results & Data Analysis

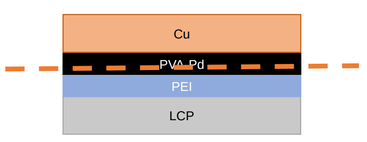
◆ Peelable Copper Foil Technology

✓ Fracture Analysis

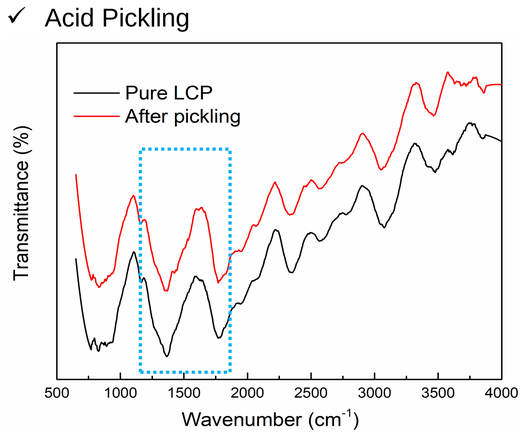




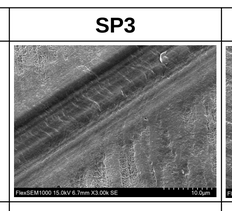
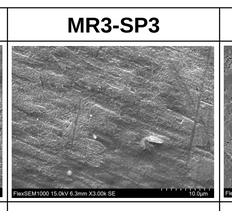
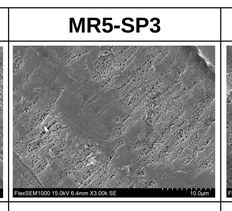




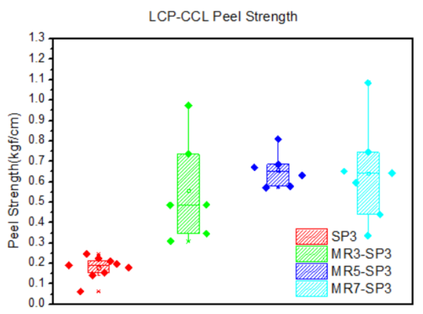
✓ Acid Pickling



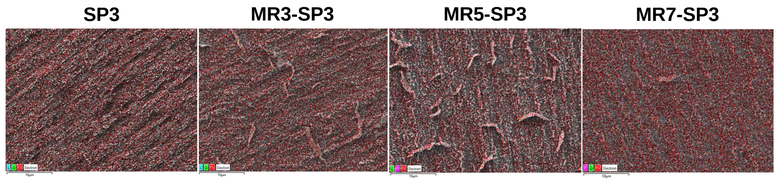
◆ Micro-Roughening (MR) Technology

	SP3	MR3-SP3	MR5-SP3	MR7-SP3
Morphology				
Roughness (μm)	Ra=0.103±0.036 Rq=0.130±0.047 Rz=0.592±0.245	Ra=0.281±0.231 Rq=0.391±0.298 Rz=1.334±1.116	Ra=0.131±0.061 Rq=0.420±0.494 Rz=0.592±0.275	Ra=0.212±0.255 Rq=0.276±0.331 Rz=1.013±1.175

✓ Adhesion Performance: T-Peeling



✓ Fracture Analysis



Element / Sample	SP3 (Atomic%)	MR3-SP3 (Atomic%)	MR5-SP3 (Atomic%)	MR7-SP3 (Atomic%)
Cu	95.5	58.5	57.2	52.0
C	4.5	37.3	38.1	44.2
O	0	4.2	4.7	3.8

Conclusions

1. **Ultra Thin Peelable Copper Foil Technology:**
   - Successfully prepared thin, peelable copper film on LCP having peeling strength ~ 30 gf/cm.
   - Fracture analysis was done to make it reusable.
   - Acid pickling can easily wash out the residues in the LCP and hence it is reusable.
2. **Via Micro-Roughening (MR) Treatment and Polymer-Capped Pd Catalyst to Achieve High Adhesion Metallization Manufacturing:**
   - Micro-roughening occurs when the surface becomes slightly rougher due to pore etching, resulting in the creation of small pores, rather than a significant increase in roughness.
   - As the duration of micro-roughening increases, more substructures are formed on the surface, leading to a higher peel force. Successfully average adhesion 0.1→ 0.6 (kgf/cm), maximum adhesion 0.2→1.0(kgf/cm).
   - Fracture analysis on Cu side shows that as the time of MR increases:
     1) The carbon and oxygen increases.
     2) More LCP was found on Cu side, indicating anchoring effect is enhanced.

Contact details: tcwei@mx.nthu.edu.tw (Tzu-Chien Wei), vidyakattoor29@gmail.com (Vidya Kattoor), ljps70703@gmail.com (Yi-Cang Wu), qweasd95421@gmail.com (Pei-Qing Yang), patty890220@gmail.com (Pei-Tsen Wei)