

POLITECNICO
MILANO 1863

Elettrodeposizione Assistita da Laser di Metalli per Impieghi Decorativi

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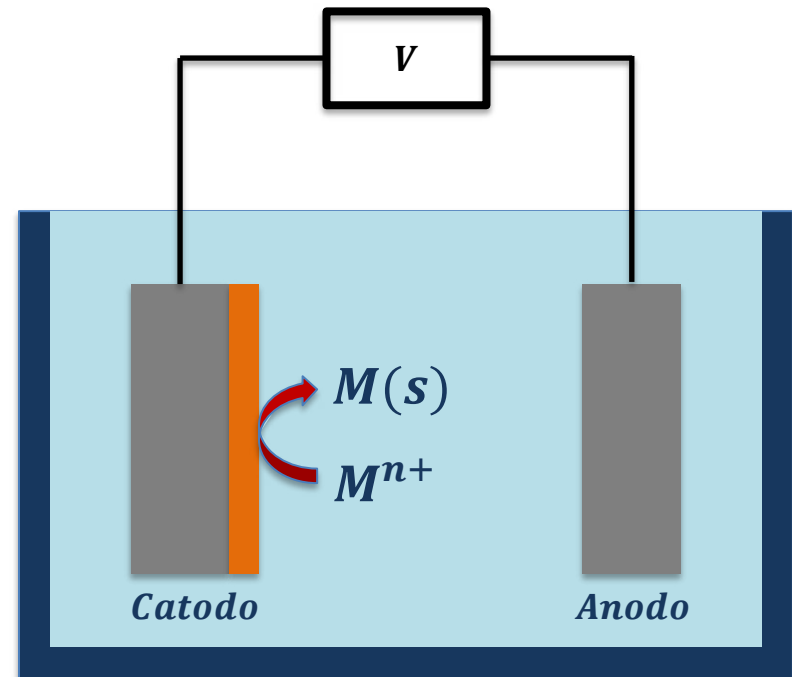
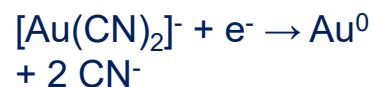
- Introduzione
- Scopo del lavoro
- Risultati
 - LAE di Pd
 - LAE di Pt
 - LAE di Au
 - LAE di leghe
 - Applicazione decorative
- Conclusioni

Elettrodeposizione di strati metallici: il processo **standard**

- Migrazione dei cationi verso l'elettrodo negativo (catodo)
- Riduzione allo stato metallico

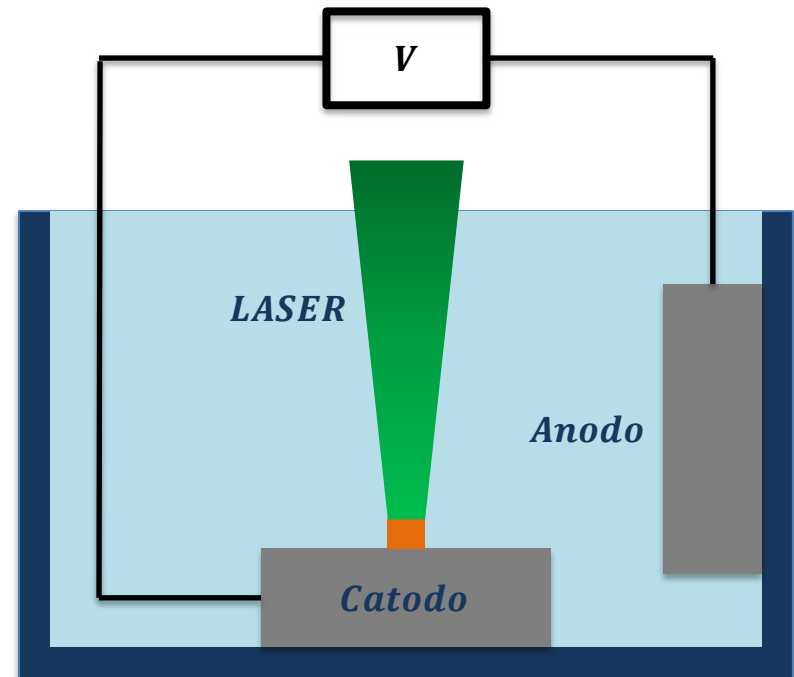
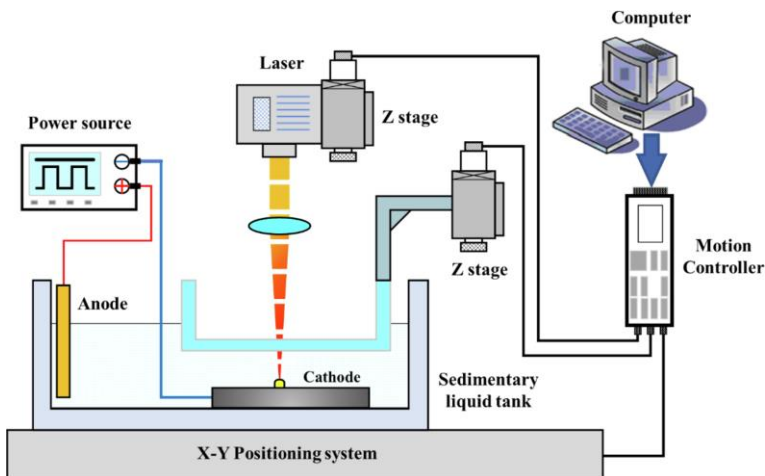


Esempio: deposizione di oro da cianuri



LASER Enhanced Electrodeposition (LEE):

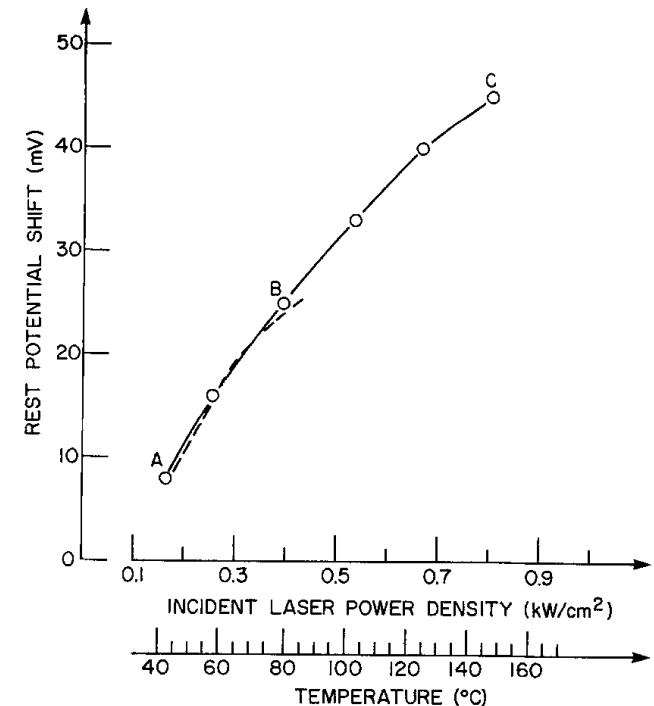
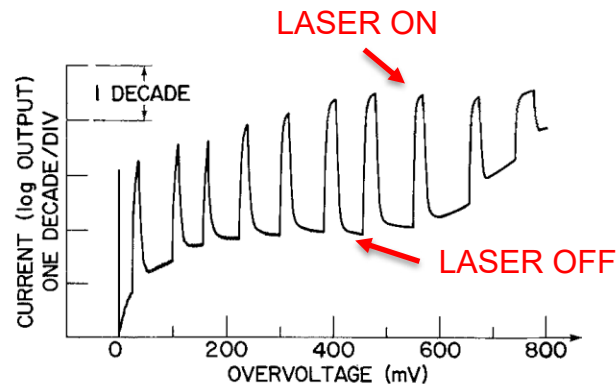
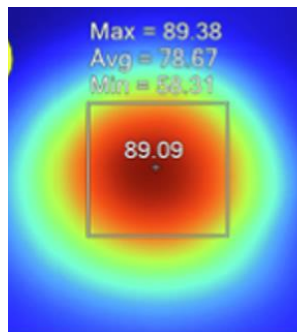
- La cella è polarizzata a bassi potenziali
- La luce LASER innesca la deposizione
- Il metallo si deposita localmente



Puippe et al., J. Electrochem. Soc. 128(12), 2539-2545 (1981)

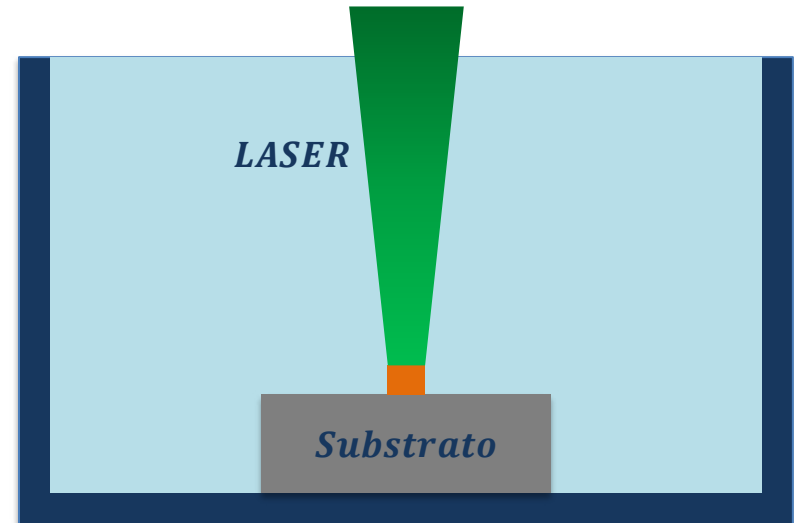
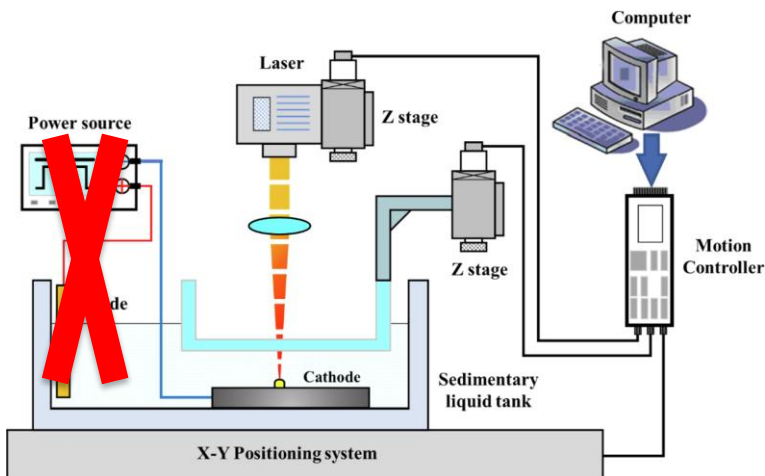
Meccanismo di deposizione LEE:

- La radiazione elettromagnetica aumenta localmente la $T \rightarrow$ aumenta l'open circuit potential (OCP) nello spot LASER
- La barriera energetica per la deposizione diminuisce



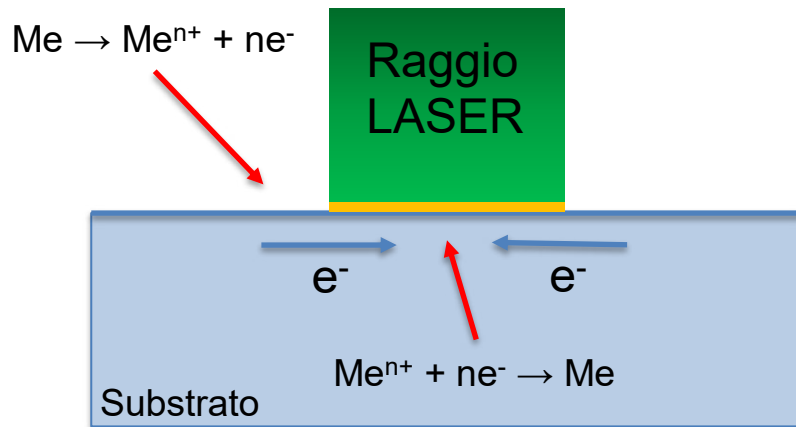
LASER Assisted Electrodeposition (LAE):

- Se la P_{LASER} è sufficientemente alta \rightarrow no polarizzazione
- La radiazione supporta completamente la riduzione
- Il metallo viene depositato selettivamente



Puippe et al., J. Electrochem. Soc. 128(12), 2539-2545 (1981)

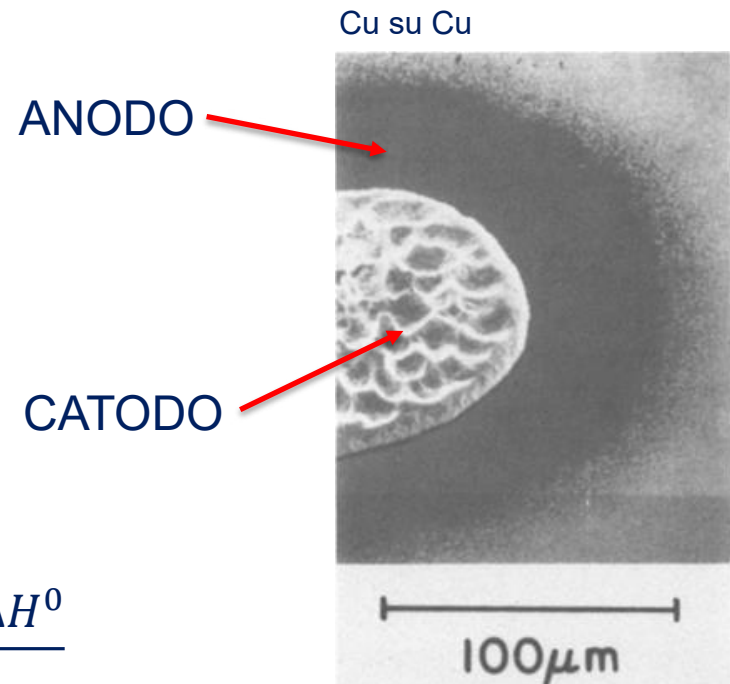
Meccanismo LAE → formazione di una cella termogalvanica:



Contributo
termodinamico:

$$-nFE^0 = \Delta G^0$$

$$\frac{d\Delta G^0}{dT} = -\Delta S^0 = \frac{\Delta G^0 - \Delta H^0}{T}$$

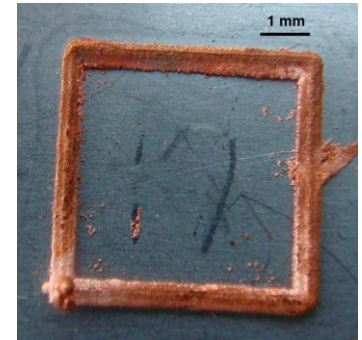


Caratteristiche applicative:

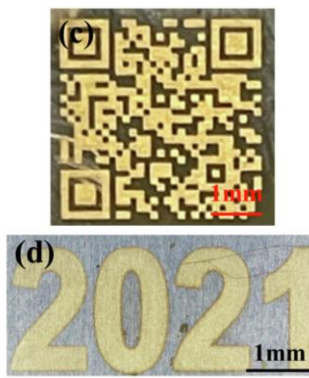
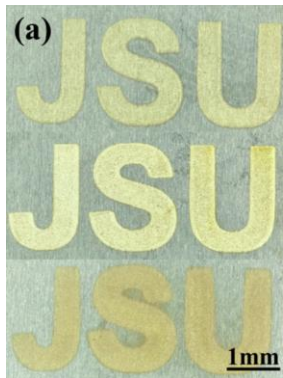
- Possibilità di patternare gli strati
- Alti ratei di deposizione
- Microstruttura peculiare → elevate proprietà meccaniche



R. Bernasconi et al., Surf. Coat. Tech. 484, 130849 (2024)



R. K. Gupta et al., Surf. Eng. 34(6), 446-453 (2017)



Guo et al., Opti. Laser Tech. 154, 108283 (2022)

Applicazioni:

- Rivestimenti estetici
- Rivestimenti antiusura
- Elettronica
- Catalisi

- Depositare strati metallici **senza** polarizzazione (LAE)

3 coppie metallo-substrato:

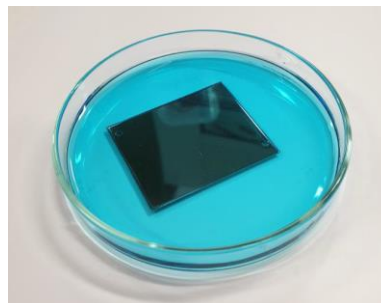
- Pd su Au
 - Pt su Au
 - Au su Pd
- Verificare l'effetto dei **parametri di processo** sulla LAE
 - Dimostrare l'applicabilità della LAE per usi **decorativi**

Setup LASER usato:

- LASER verde a fibra (532 nm)
- 100 W (max)
- Operato in QCM

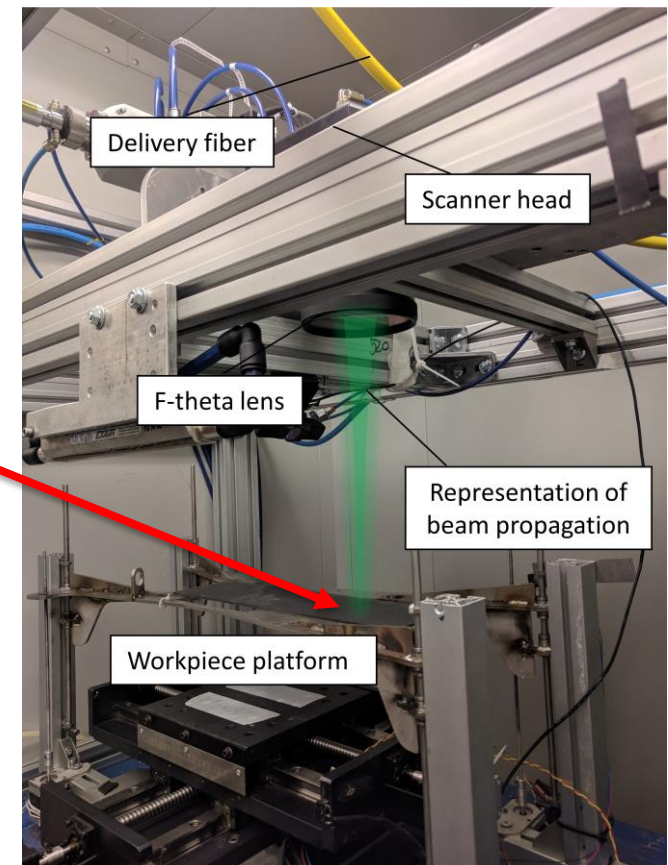
Parametri di processo:

- Potenza ottica (**P**)
- Velocità di scansione (**v**)
- Densità di linee (**H**)
- Numero di passate (**N**)



Substrati:

- Alpacca placcata Pd
- Alpacca placcata Au



Elettroliti:

- Analoghi ai bagni da elettrodeposizione

Pt:

- 500 mM ammonio idrogeno fosfato
- 5 mM Sale P
- pH 7 con NaOH

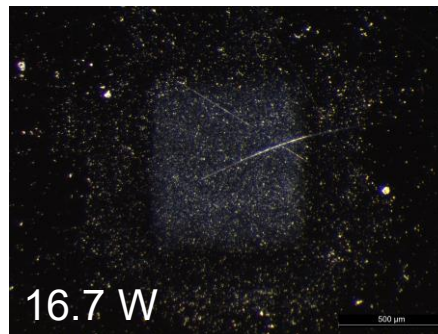
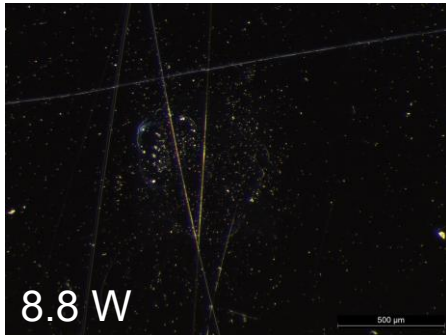
Pd:

- 500 mM ammonio idrogeno fosfato
- 5 mM palladio cloruro
- pH 8 con NH_4OH

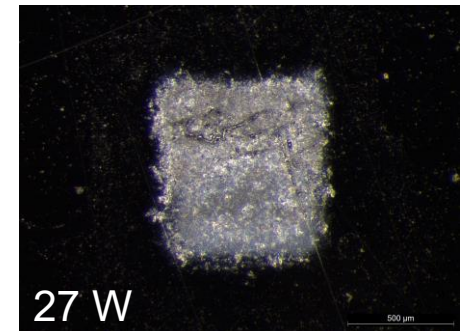
Au:

- Elettrolita solfito - tiosolfato

Pd su Au ($H = 50 \mu\text{m}$, $N = 1$, $v = 0.1 \text{ mm/s}$):

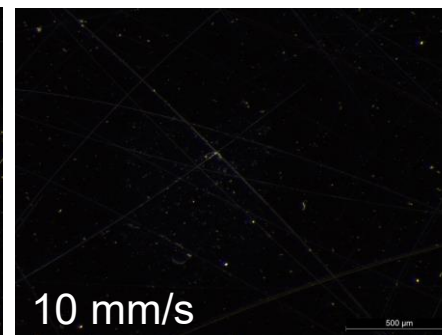
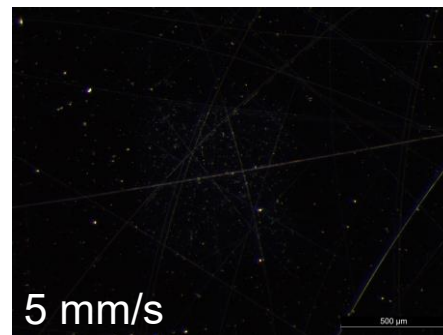
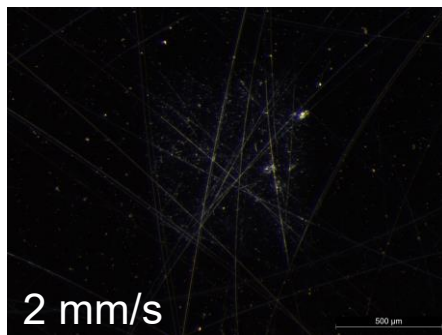
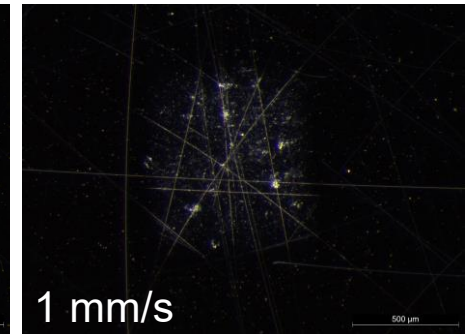
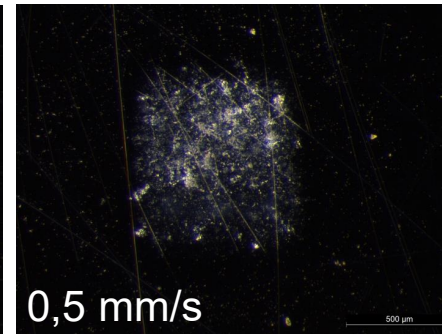
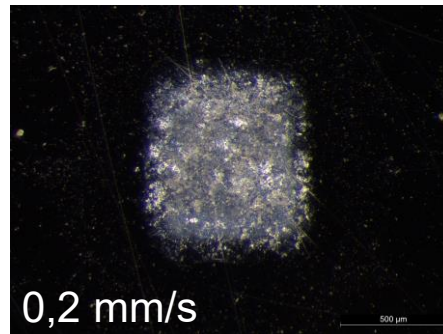
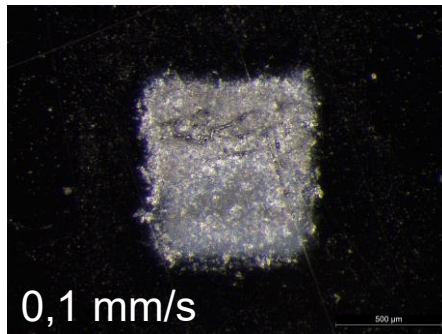


Lo spessore del
deposito aumenta
con la potenza



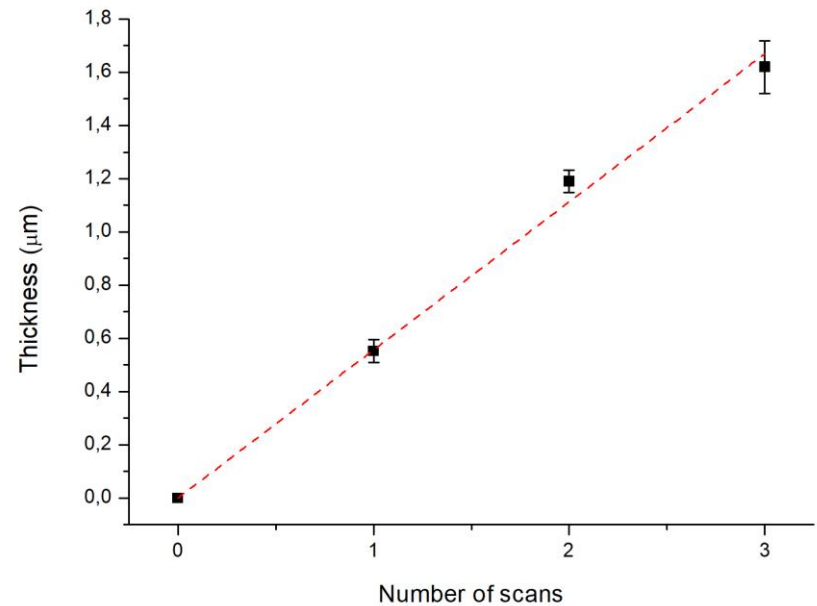
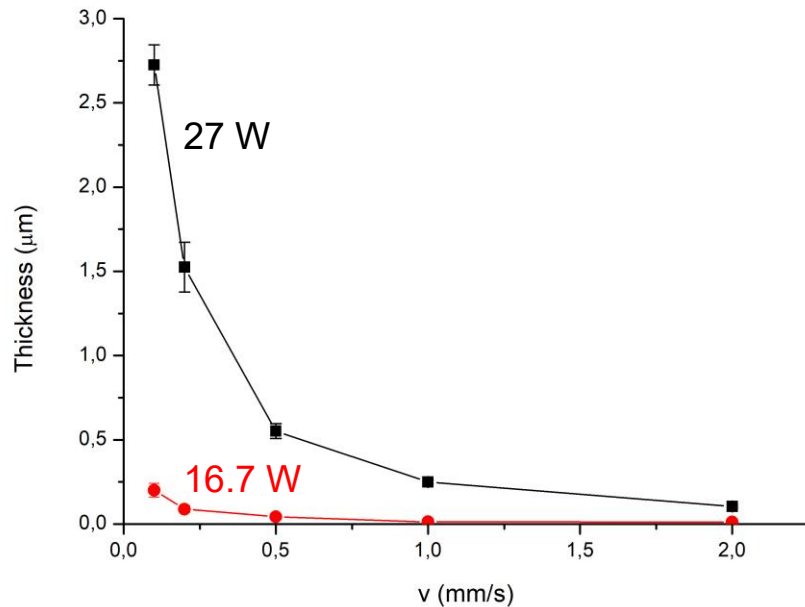
Effetto della **P** usata

Pd su Au ($P = 27 \text{ W}$, $H = 50 \text{ }\mu\text{m}$, $N = 1$):

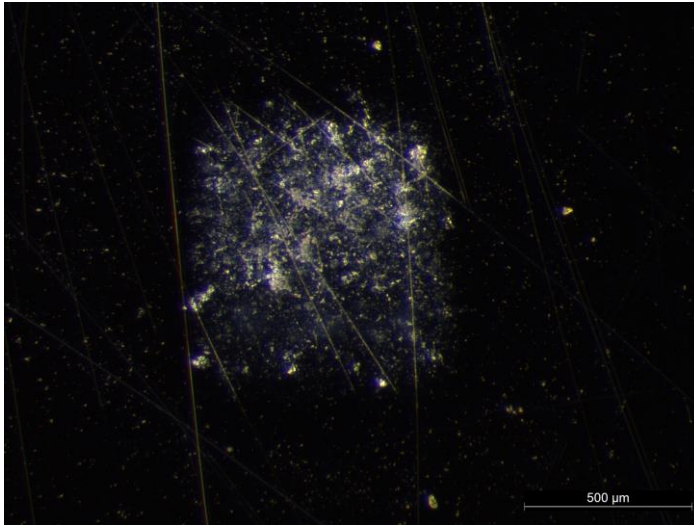


Lo spessore del deposito cala con l'aumentare della velocità

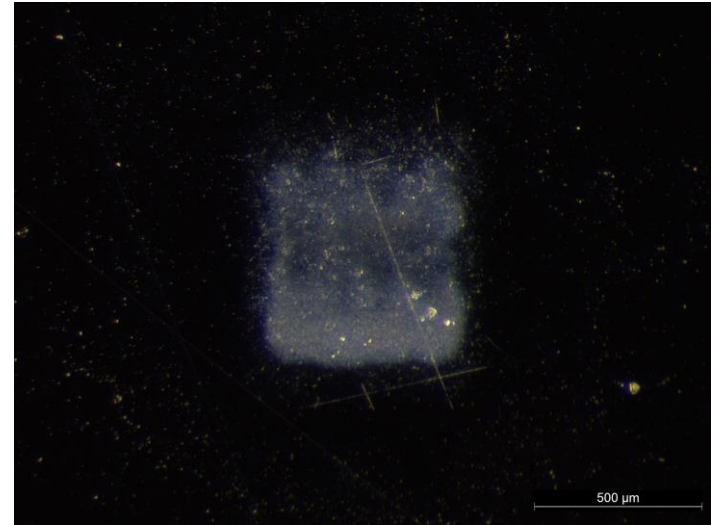
Spessore vs. v , P or N ($H = 50 \mu\text{m}$):



Spessore vs. **H** ($P = 27$ W, $N = 1$):

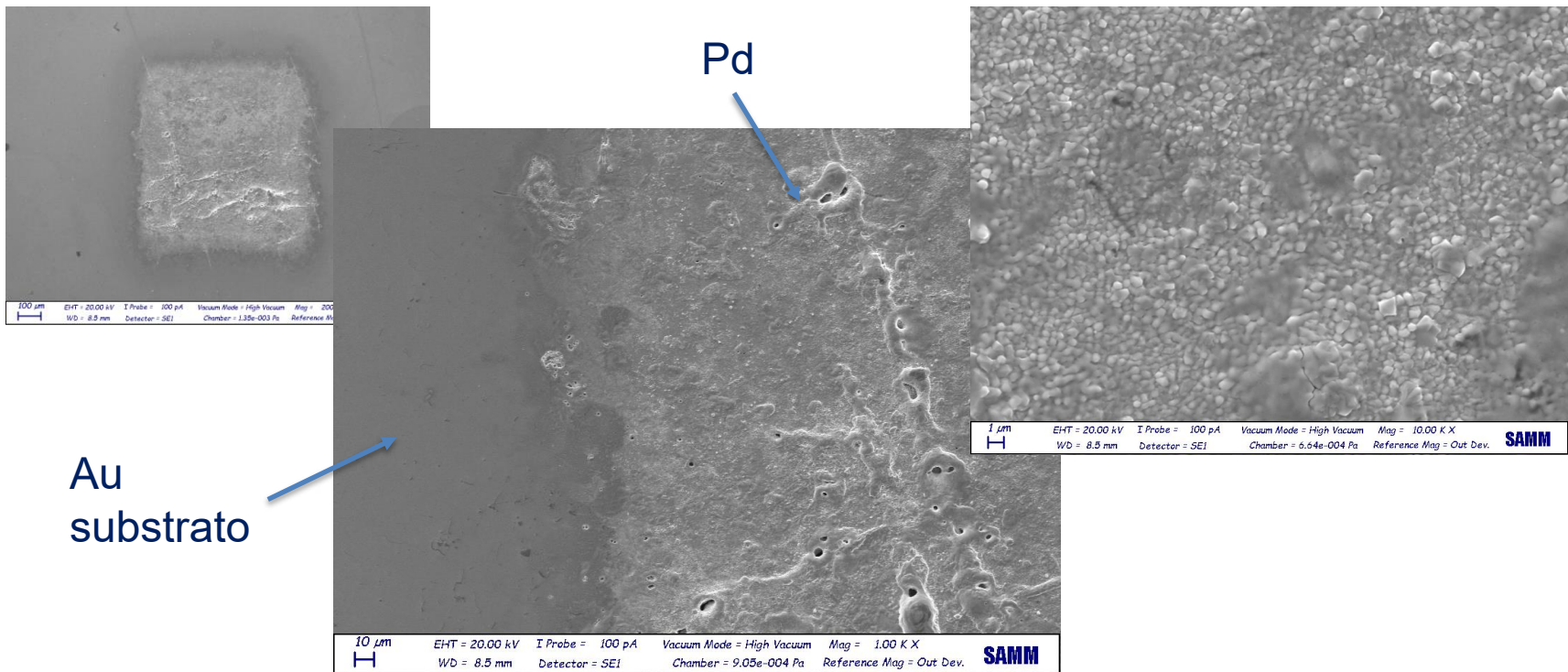


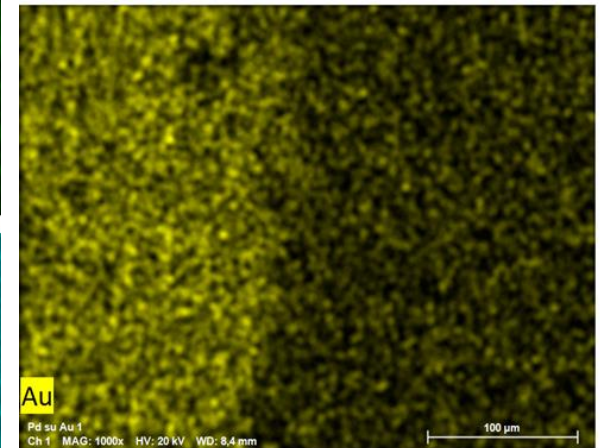
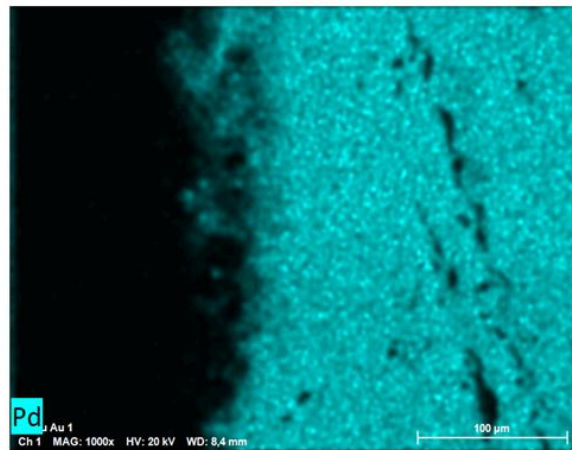
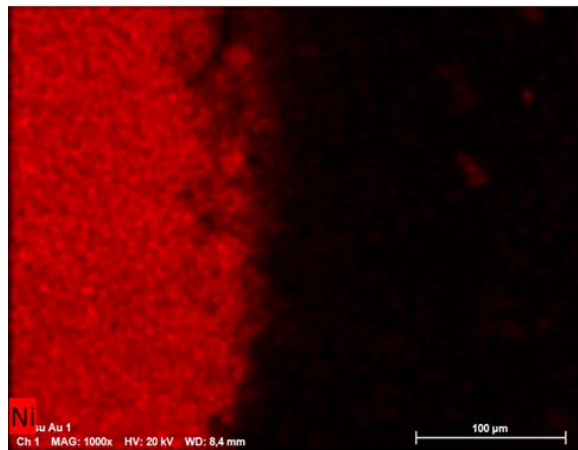
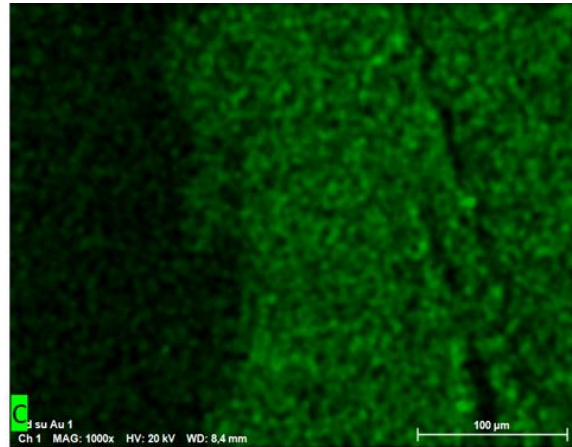
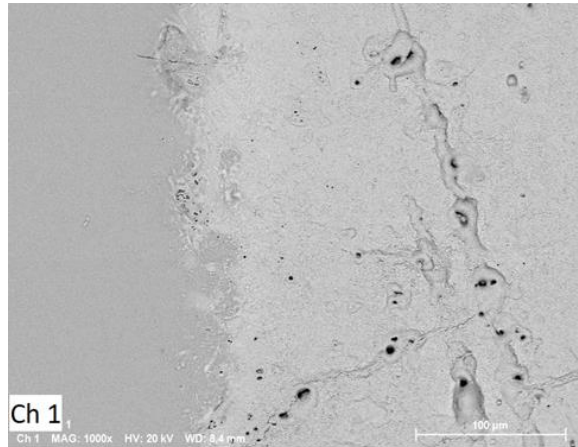
$H = 50 \mu\text{m}$; $v = 0.5 \text{ mm/s}$
Spessore = $0.55 \mu\text{m}$



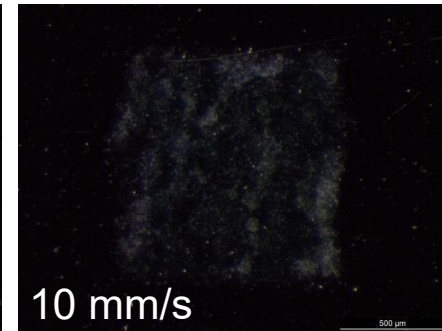
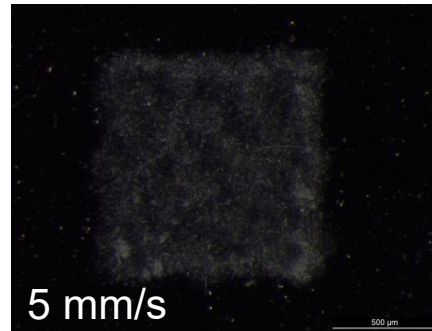
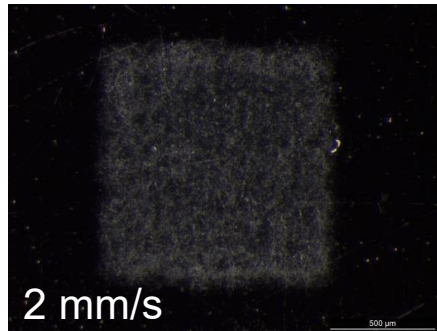
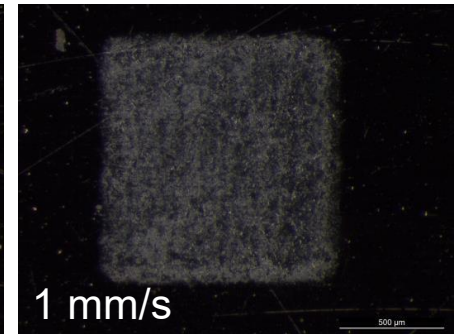
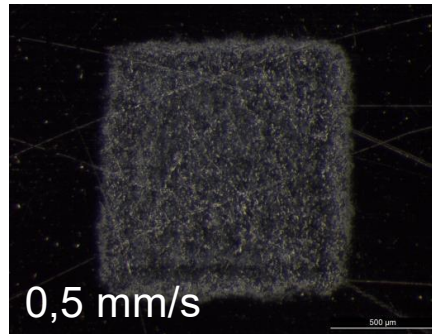
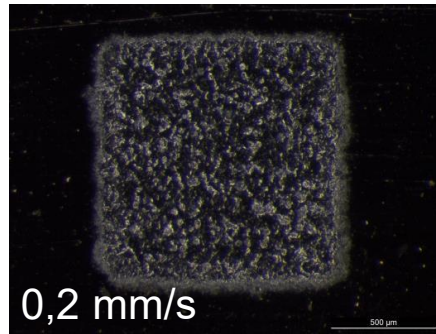
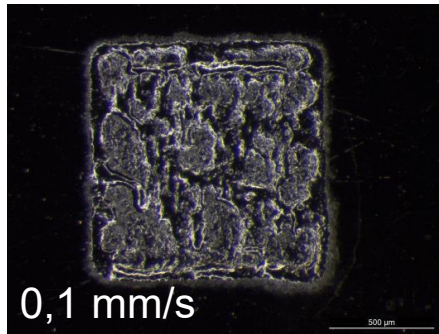
$H = 25 \mu\text{m}$; $v = 0.5 \text{ mm/s}$
Spessore = $1 \mu\text{m}$

Morfologia **SEM** (P = 27 W, H = 50 μm , v = 0.1 mm/s):

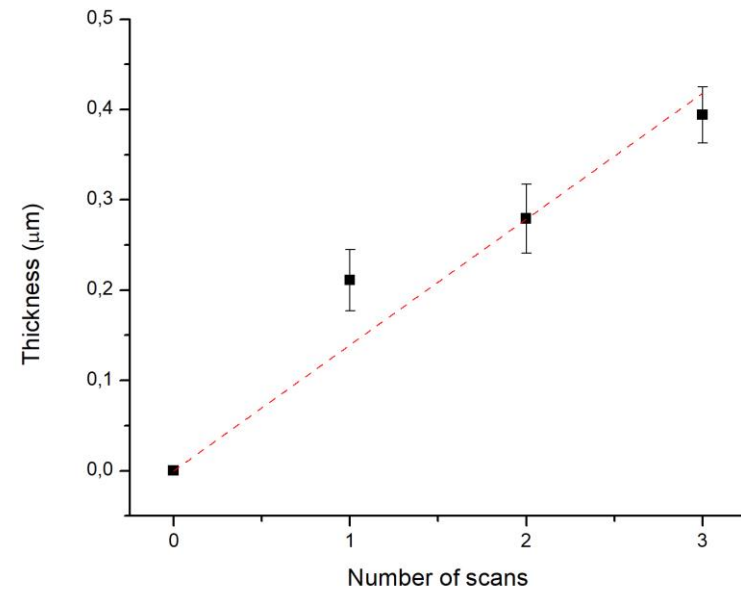
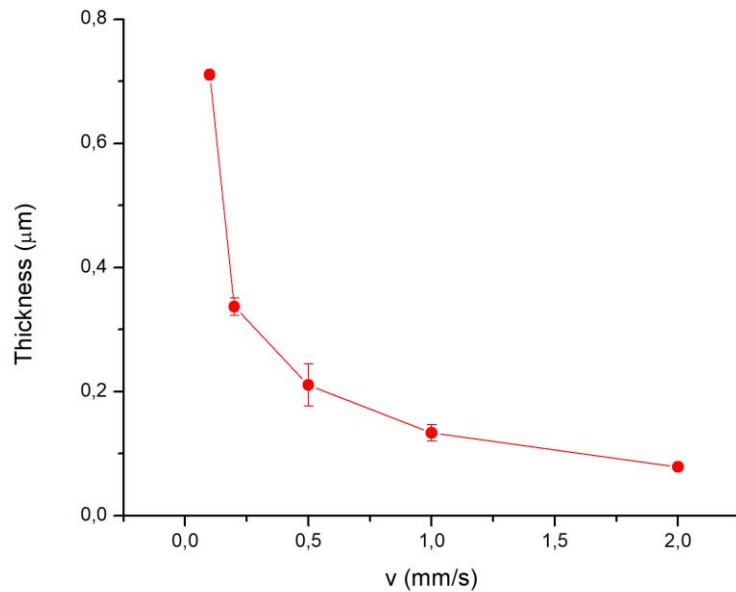




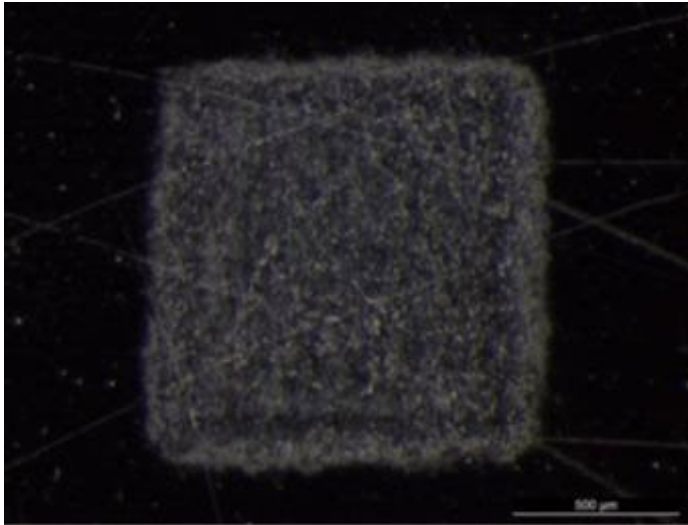
Pt su Au ($P = 27$ W, $H = 50$ μm , $N = 1$):



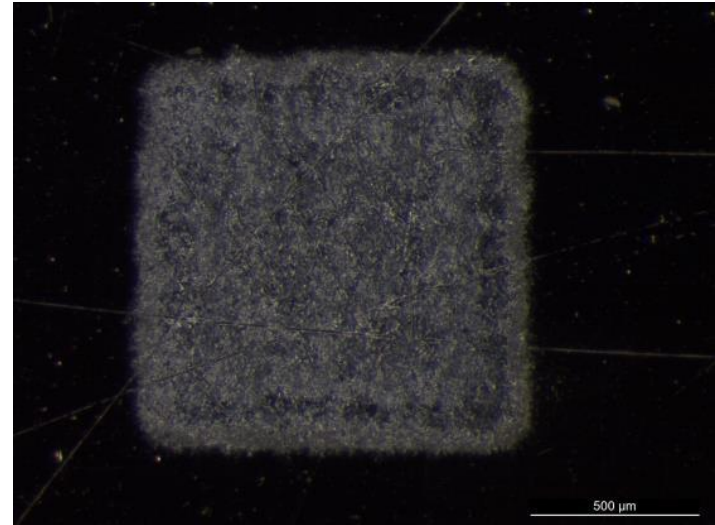
Spessore vs. v or N ($P = 27$ W, $H = 50$ μm):



Spessore vs. **H** ($P = 27$ W, $N = 1$):

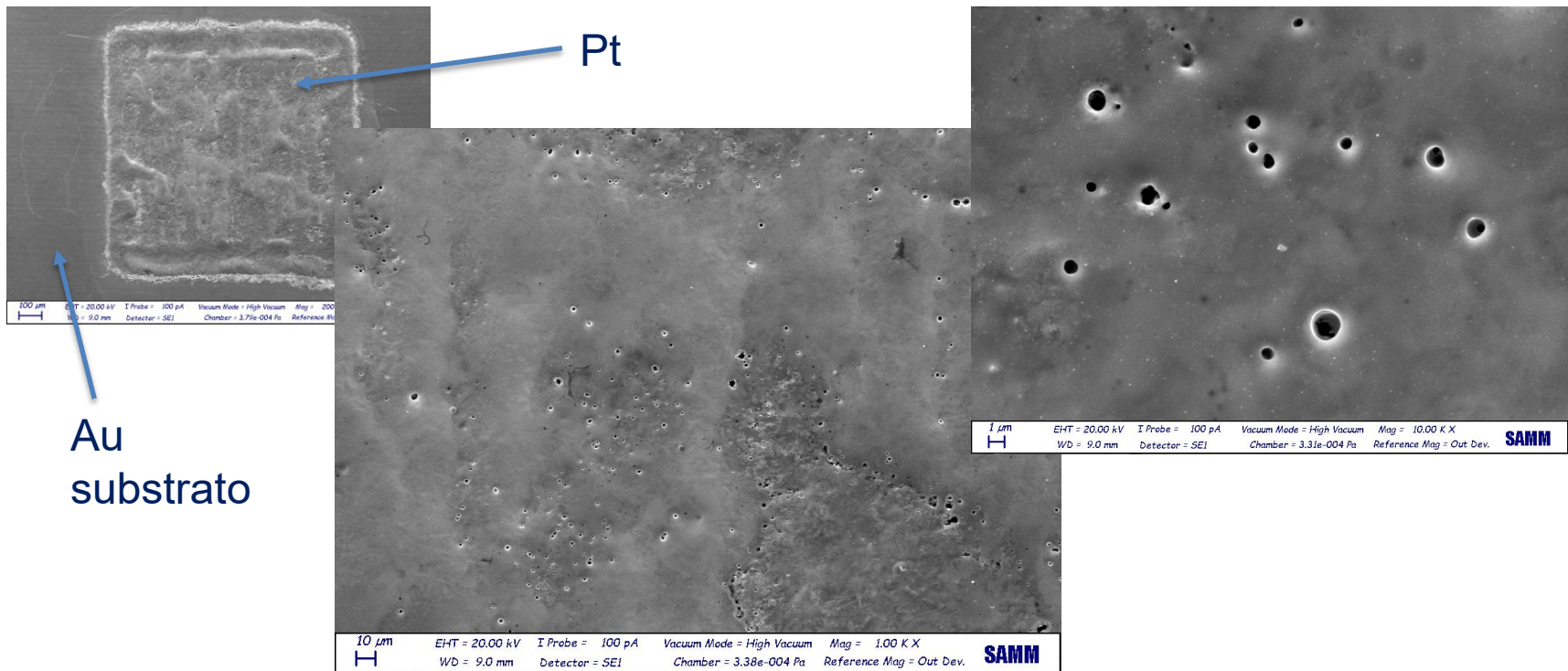


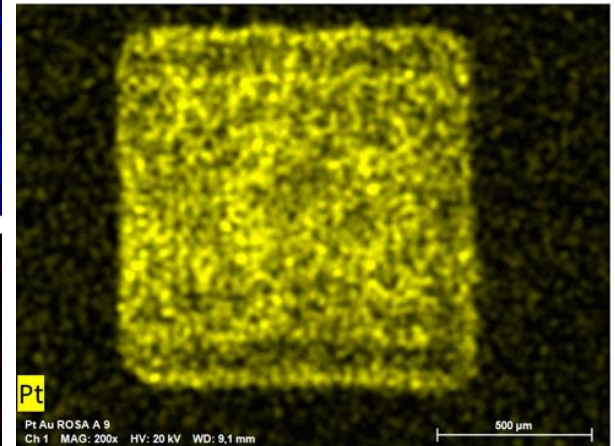
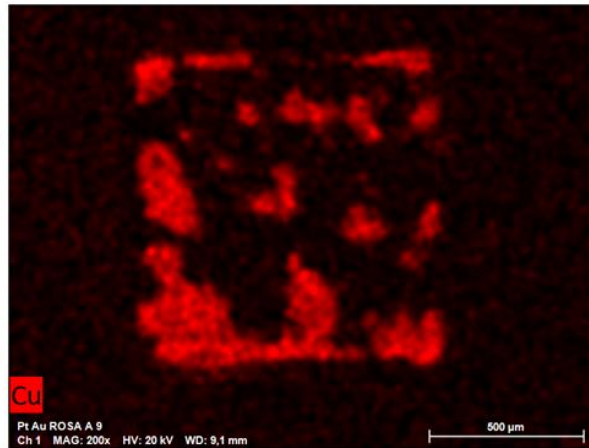
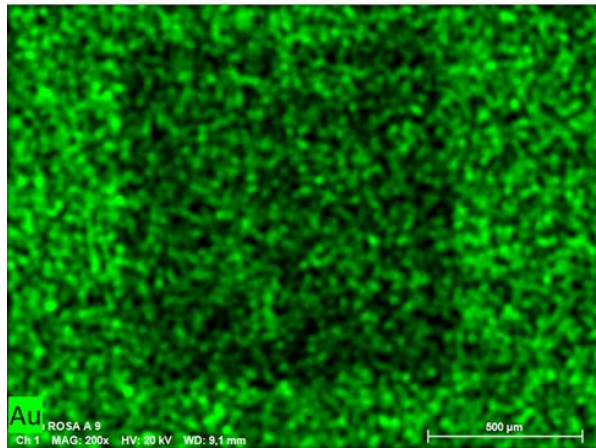
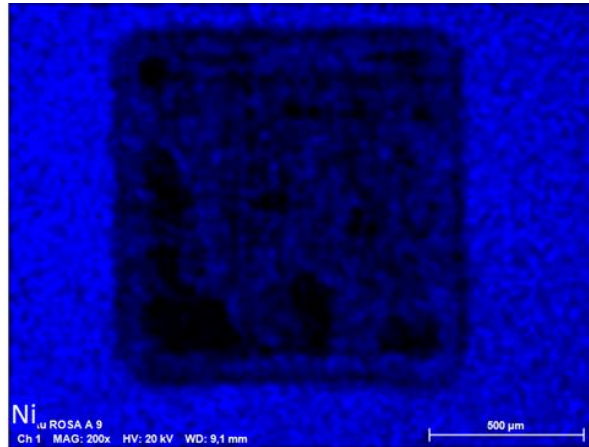
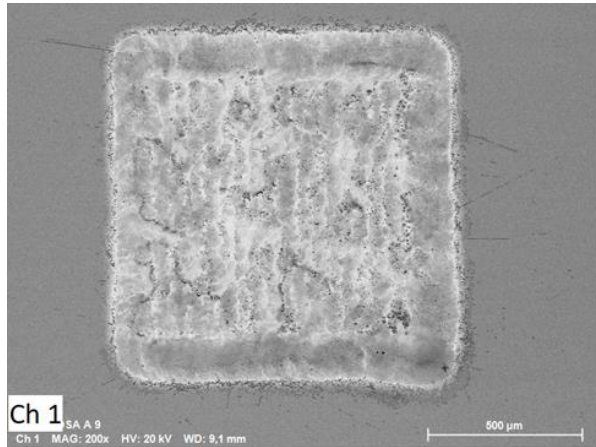
$H = 50 \mu\text{m}$; $v = 0.5 \text{ mm/s}$
Spessore = $0.211 \mu\text{m}$



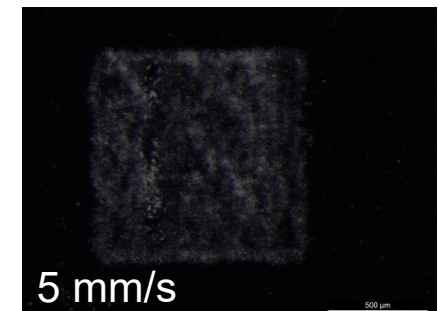
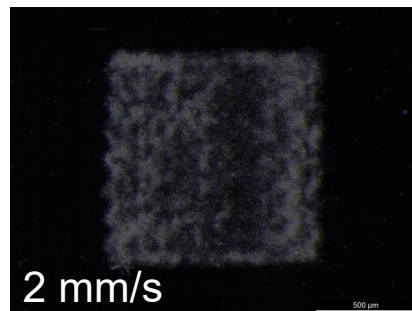
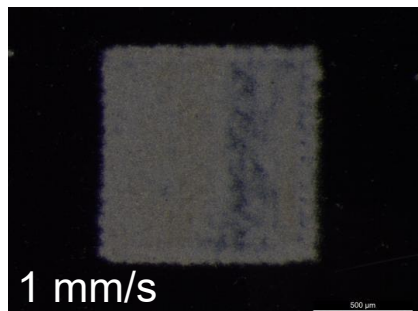
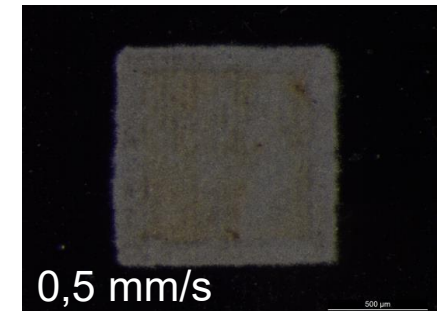
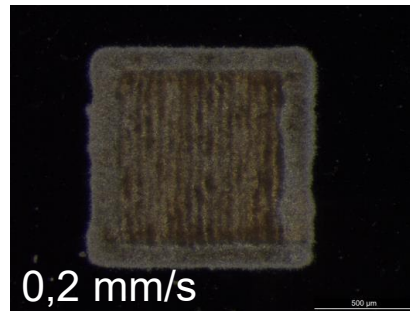
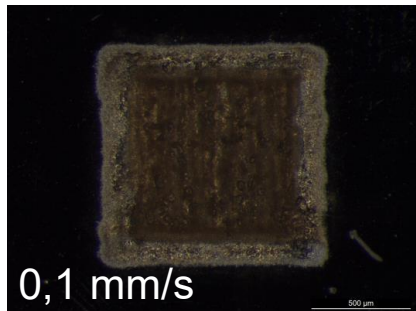
$H = 25 \mu\text{m}$; $v = 0.5 \text{ mm/s}$
Spessore = $0.331 \mu\text{m}$

Morfologia **SEM** (P = 27 W, H = 50 μm , v = 0.1 mm/s):

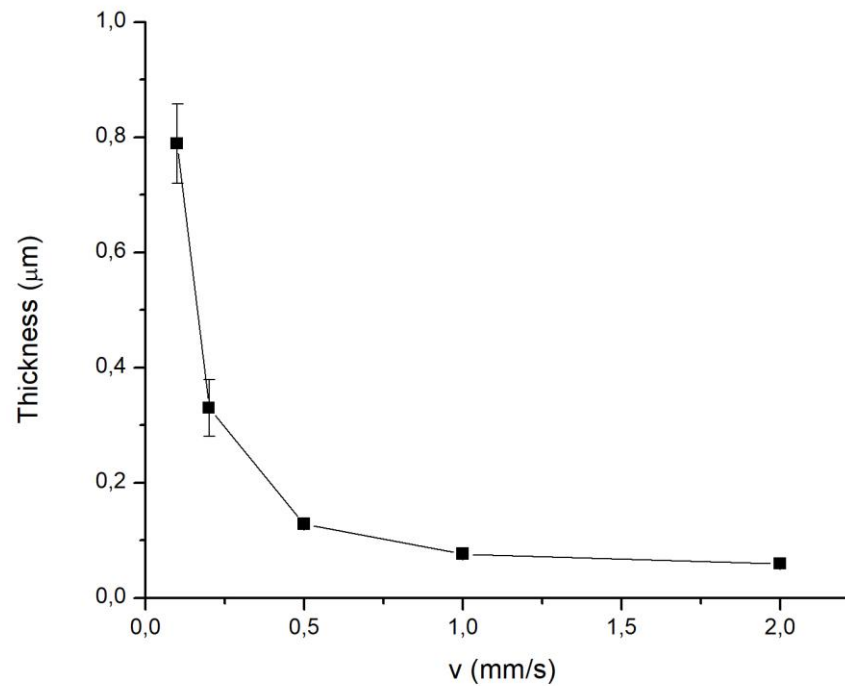




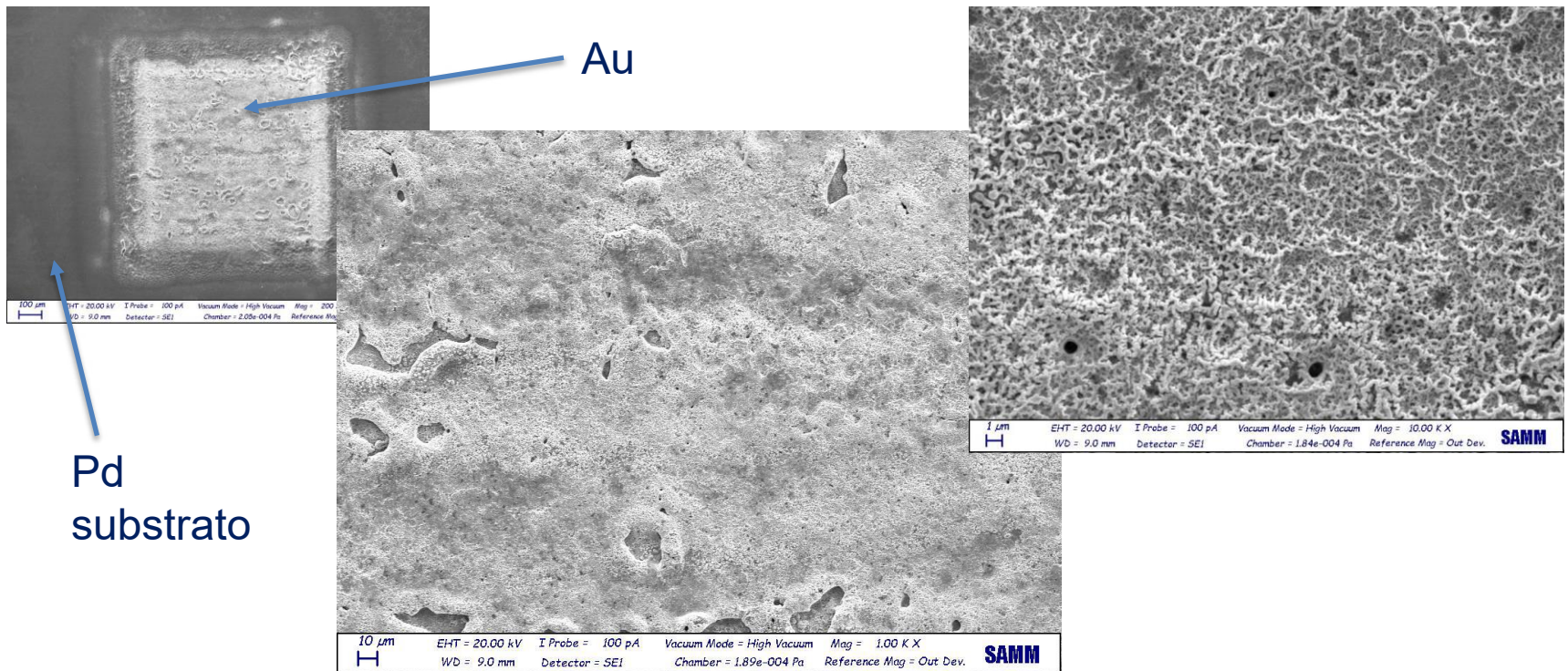
Au su Pd:

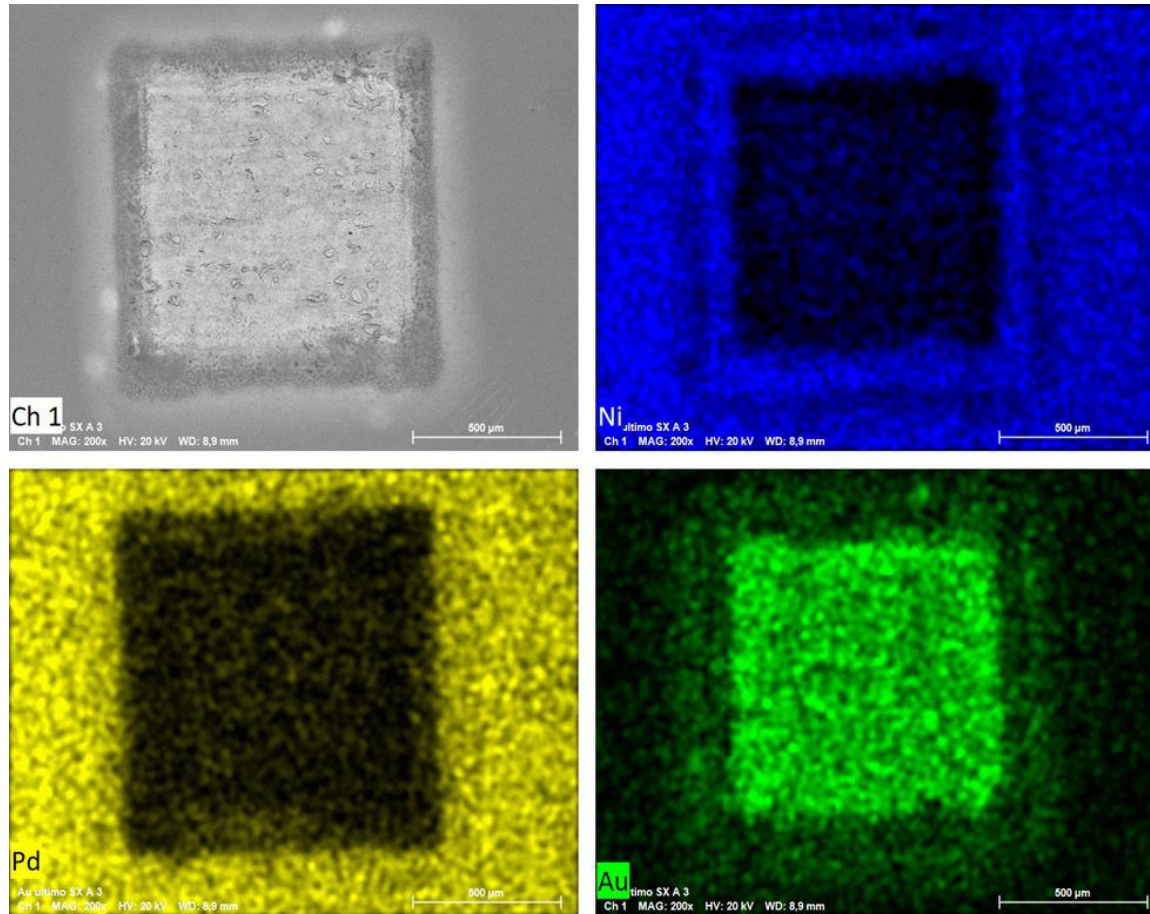


Spessore vs. v :

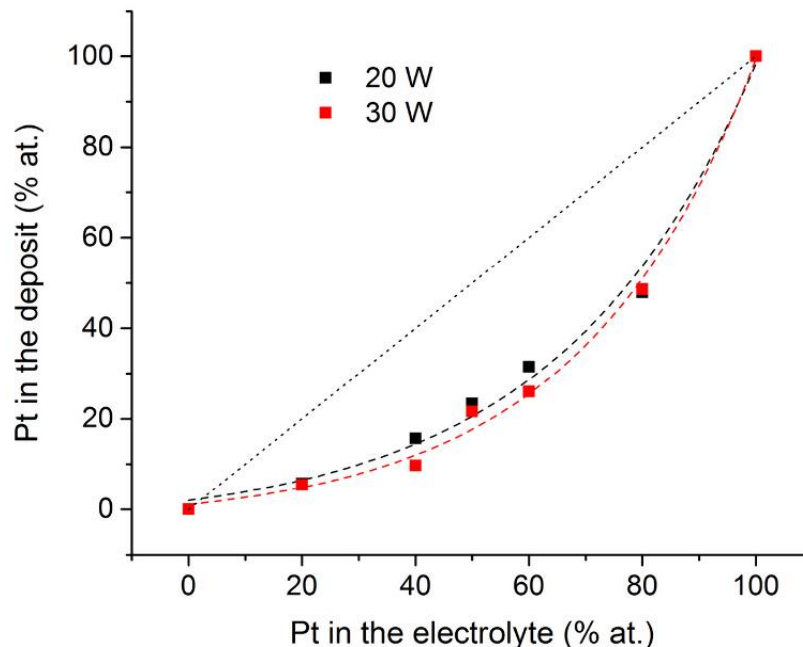


Morfologia SEM:



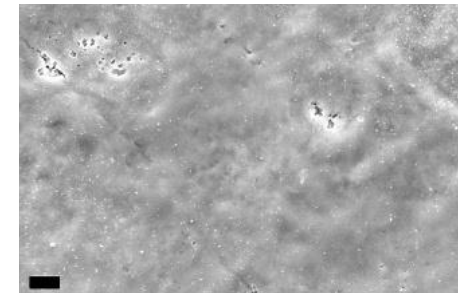


Elettrodeposizione di **leghe** metalliche: il caso del **PdPt**

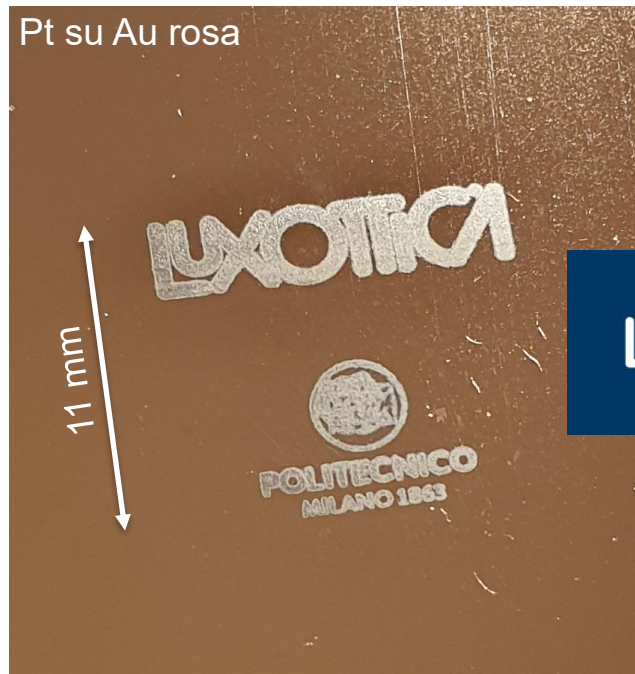


Deposizione di PdPt nell'intervallo 0 - 50 % at.

- Composizione controllabile
- Morfologia liscia
- Patternabili



Patterning su **montature per occhiali** Luxottica:



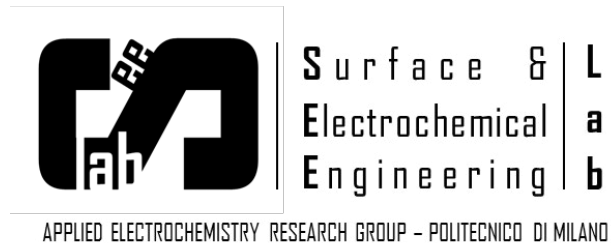
Patterning su **montature per occhiali** (Pd on Au):



Patterning su **montature per occhiali** (Pd on Au):



- Lo studio effettuato dimostra che la LAE di metalli preziosi quali Pt, Pd e Au è possibile
- Sono stati ottenuti strati uniformi su substrati di Au e Pd
- La LAE di leghe è stata dimostrata per la prima volta
- Si è dimostrato il patterning controllato di strati metallici
- La LAE di Pd su Au è stata applicata con successo al patterning di loghi su montature per occhiali



Grazie per la vostra attenzione!



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