Berner Fachhochschule
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Plasmonic Coloring of Noble Metals by Direct Laser Marking

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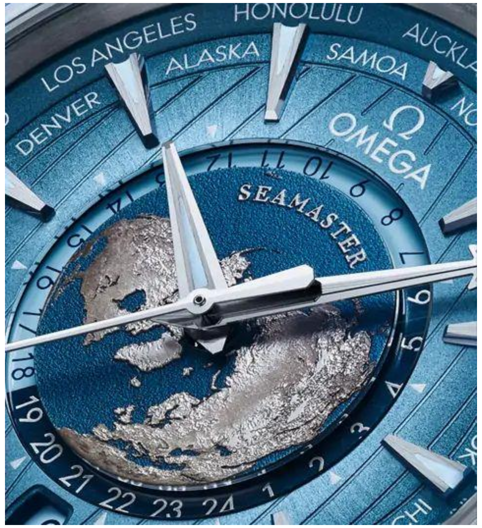
Motivation for Plasmonic Colors

- **Watches and Silver Coins**
- Metal coloring works on stainless steel, titanium, aluminum
- Oxide layer thickness determines color
- Most laser-colored surfaces are angle-dependent



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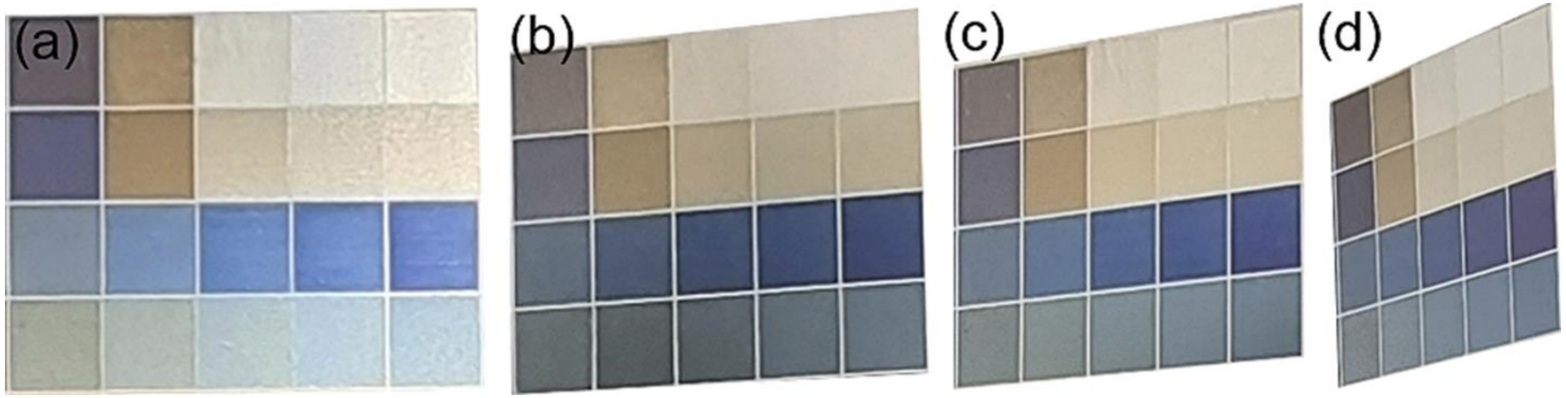

Array of colours by laser colouring on stainless steel. (a) Stainless steel sample at rest position at 0◦; (b) stainless steel sample tilted by 10◦; (c) stainless steel sample tilt

Source: Gaidys et al., Optics & Laser Technology 174 (2024) 110561

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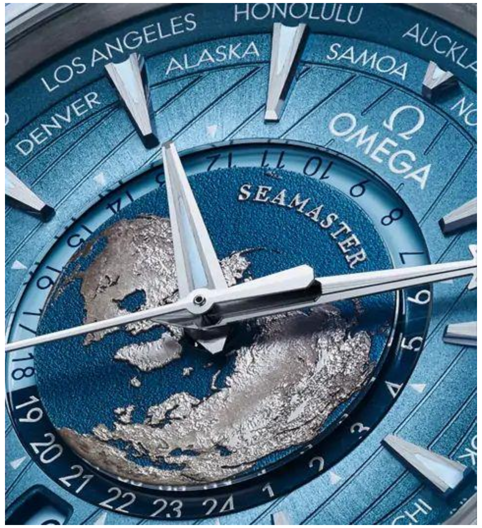
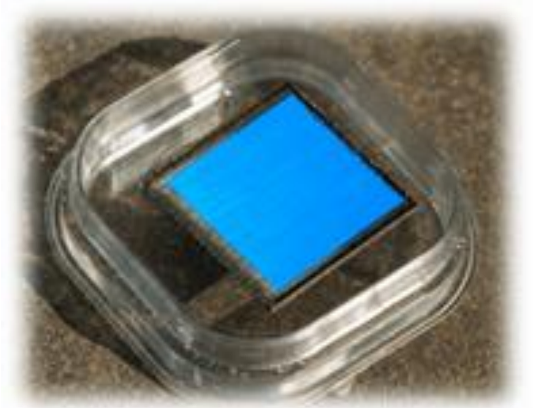
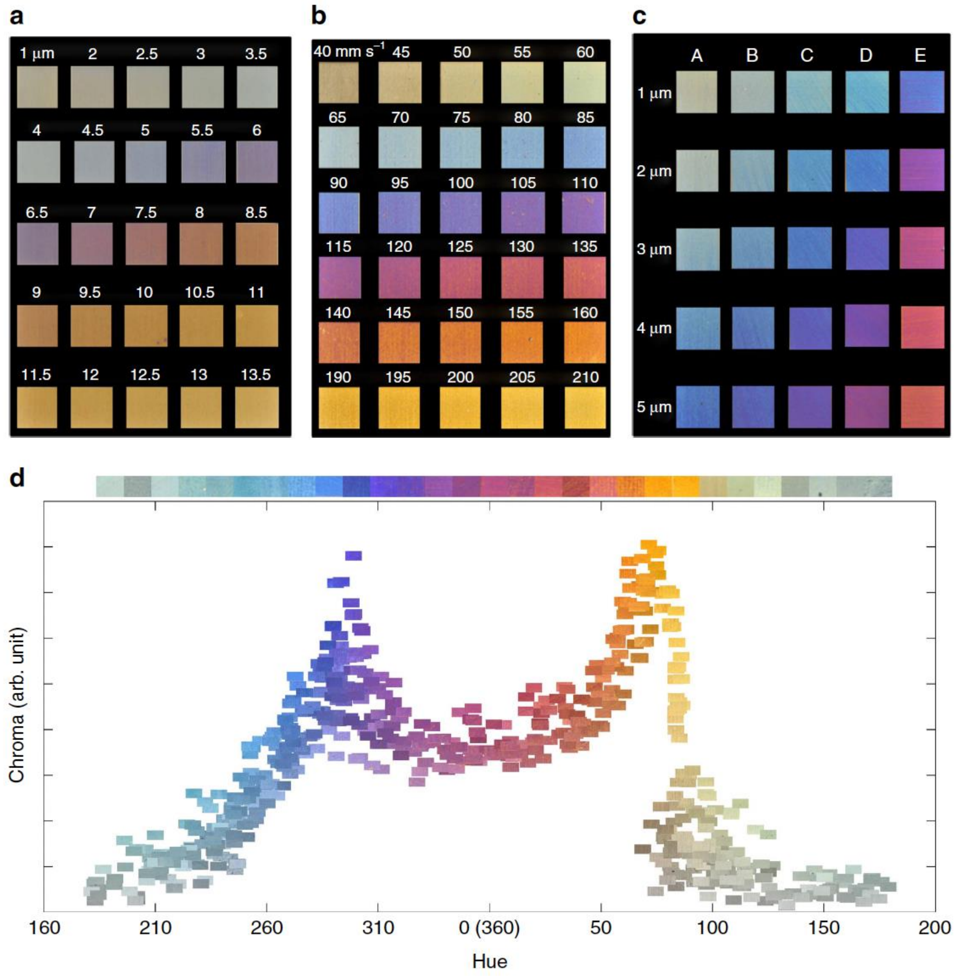




Obtainable Color Spectrum in Silver

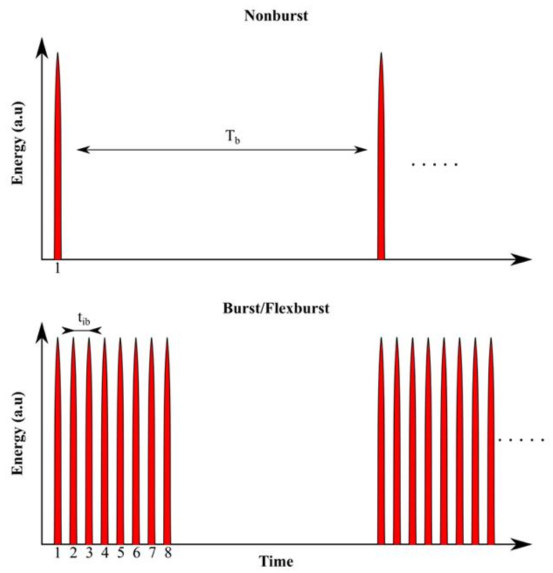
- The creation metal NPs for surface coloring has attracted considerable interest
- Guay et al results from 2016:
- A: non-burst mode
- B: burst mode
- C: variation of line spacing and hatch
- D: obtainable hue and chroma values

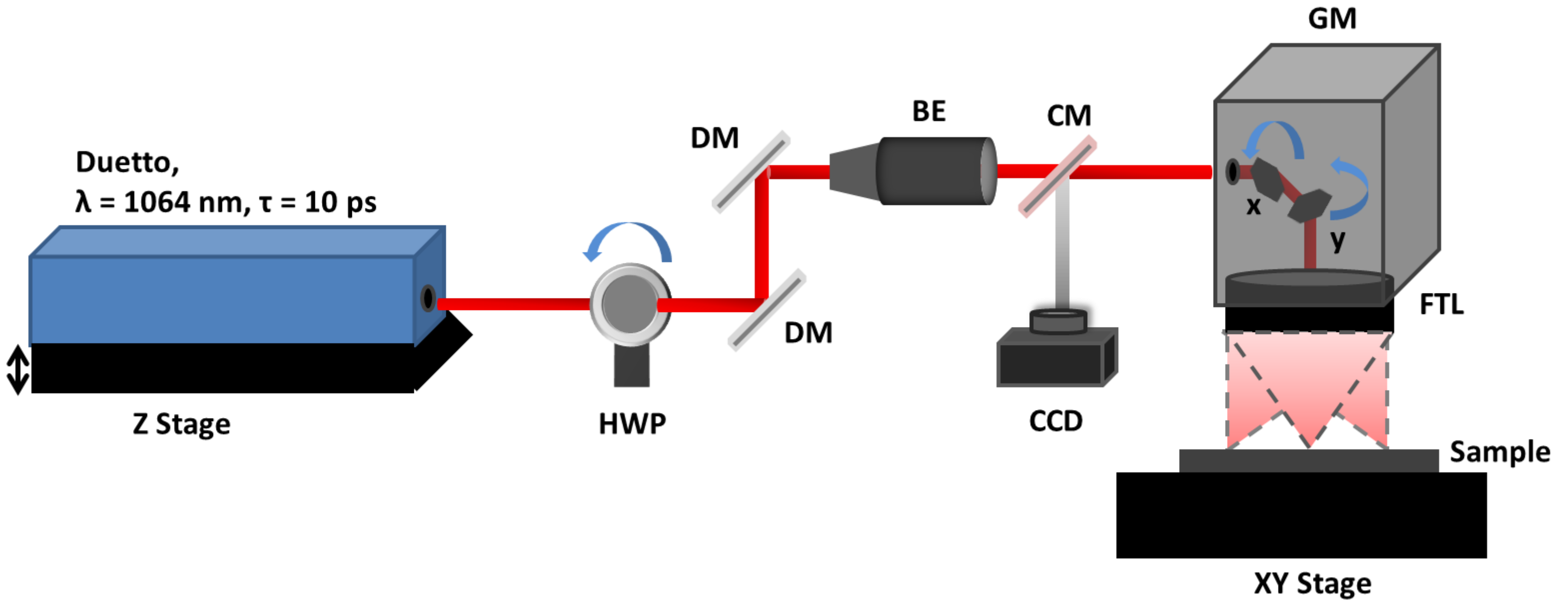


Source: https://doi.org/10.1038/ncomms16095

Previous Literature Results

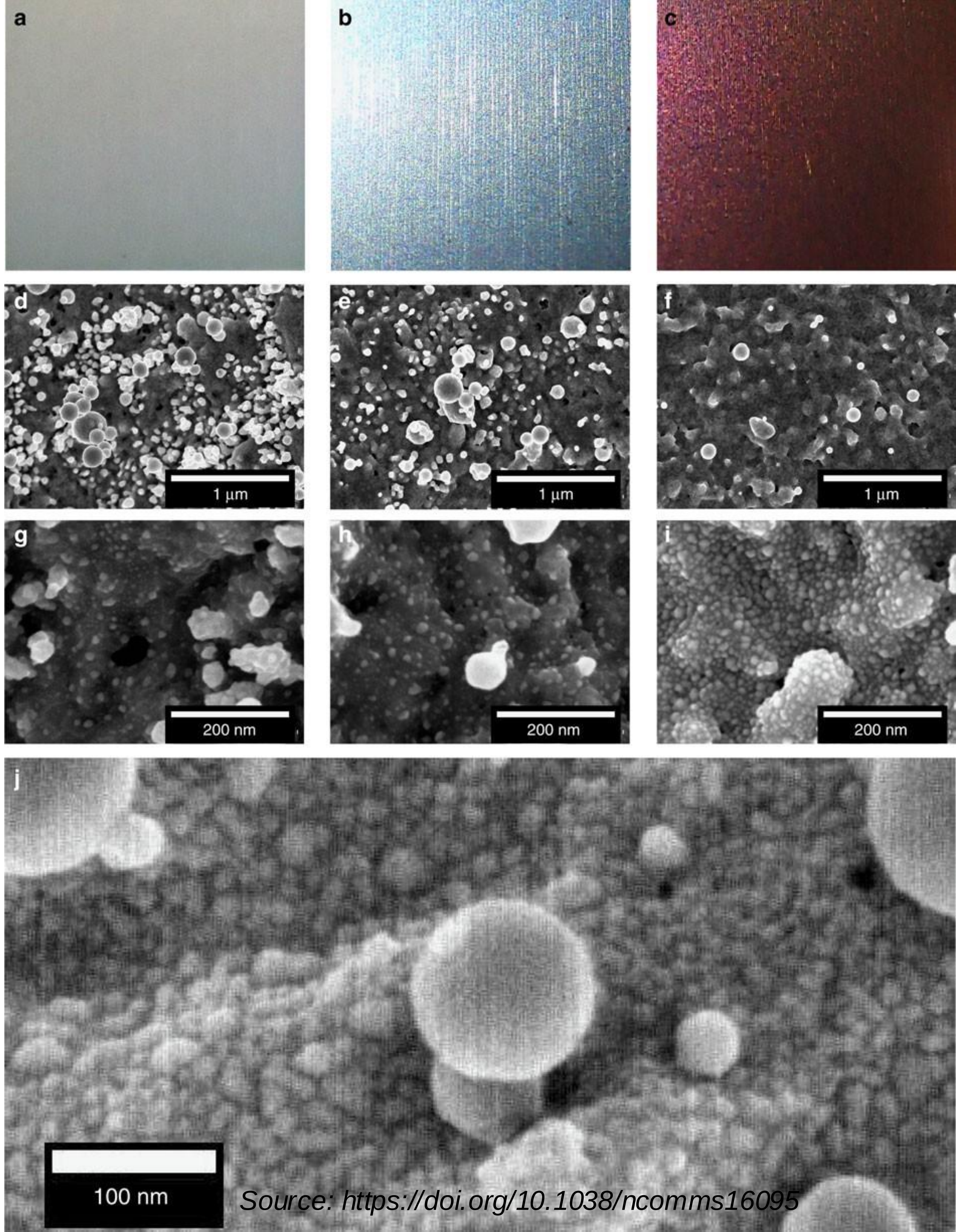
- Plasmonic resonances of metallic nanoparticles (NP) are known for colored glasses since antiquity.
- On metal surface not yet exploited for commercial use.
- Picosecond laser pulses produce non-iridescent colors on silver, gold, copper etc.
- Burst mode provides bright colors





The burst mode effect on NPs

- First pulse basically ablates material (low to no recast)
- 2nd pulse in burst pushes back particle plume to form NPs on surface
- Balance of pulse energy and pulse overlap controls size, embedding and density of NPs on surface
- NPs are a necessary but not sufficient condition for surface coloring



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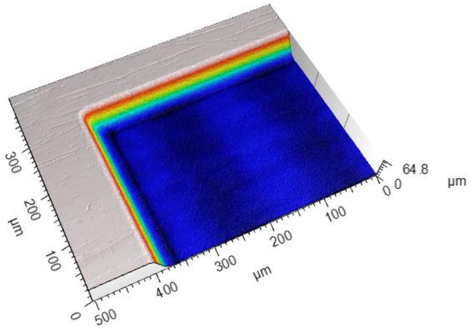
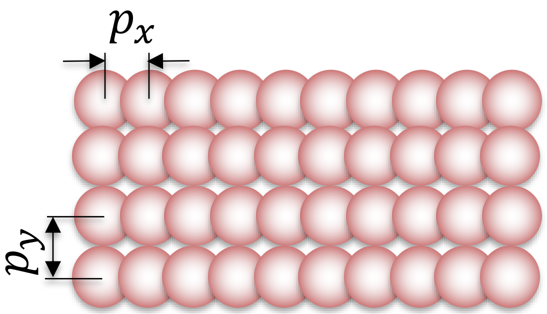
Protocol



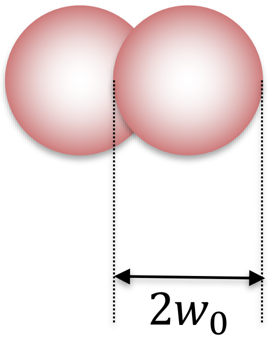
- Squares of side length $s = 3mm$ (Ag) and 5mm (Cu) machined with fine variation of spot and line distance $p_x = p_y = 1 - 20\ \mu m$.

:

- p_y is also called line distance or line pitch



- We define as overlap O between two pulses:



$$O = 1 - \frac{p_x}{2w_0} \quad \rightarrow \quad \frac{p_x}{2w_0} = (1 - O)$$

- For the marking speed follows:

$$v_{mark} = f_{rep} \cdot p_x = 2 \cdot w_0 \cdot (1 - O) \cdot f_{rep}$$

- $p_x = f_{rep}/v_{mark}$

Influence of burst mode and pitch

f_{rep} = 50kHz
p_x = 0.25µm
Φ_{tot} = 2.6 J/cm²

Discrepancy: Higher # of burst pulses do not result in brighter colors.

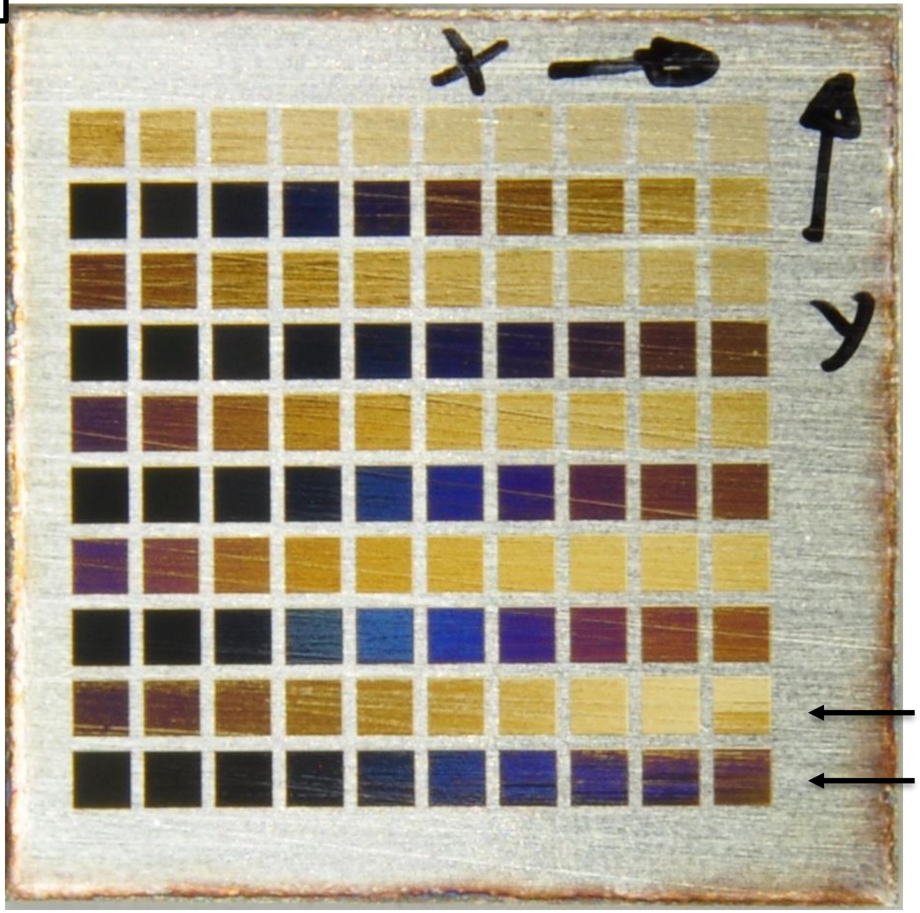
fixburst#7

fixburst#6

fixburst#4

fixburst#3

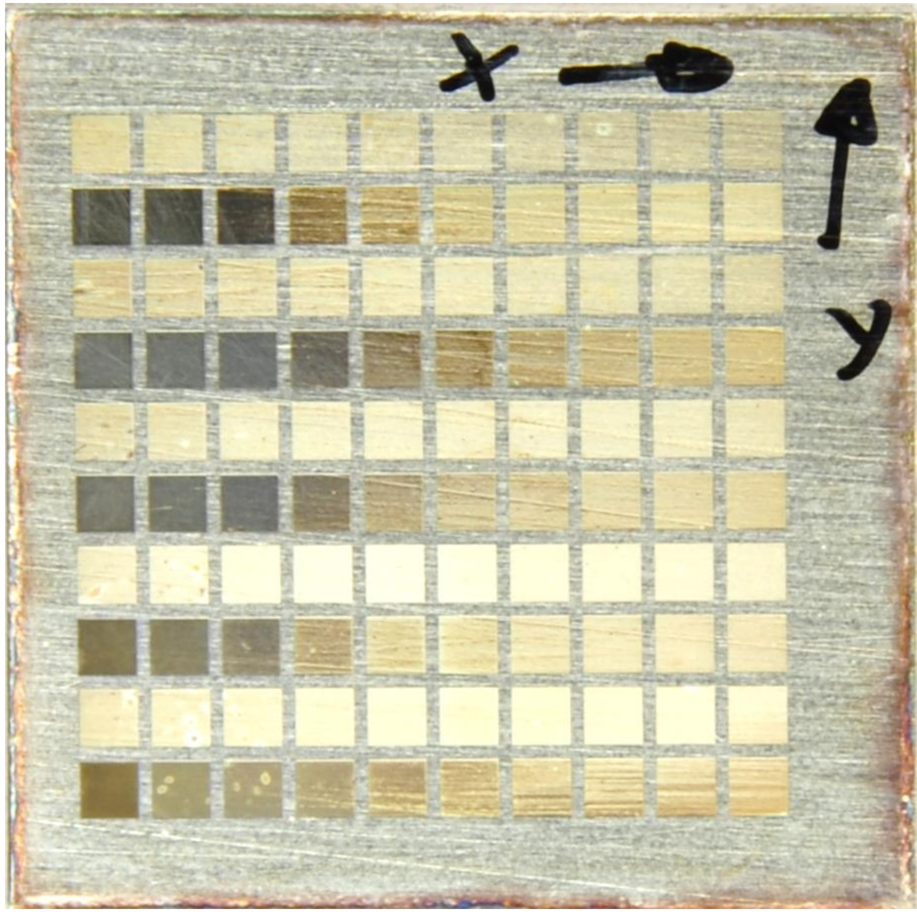
fixburst#2



p_y = 11-20µm

p_y = 1-10µm

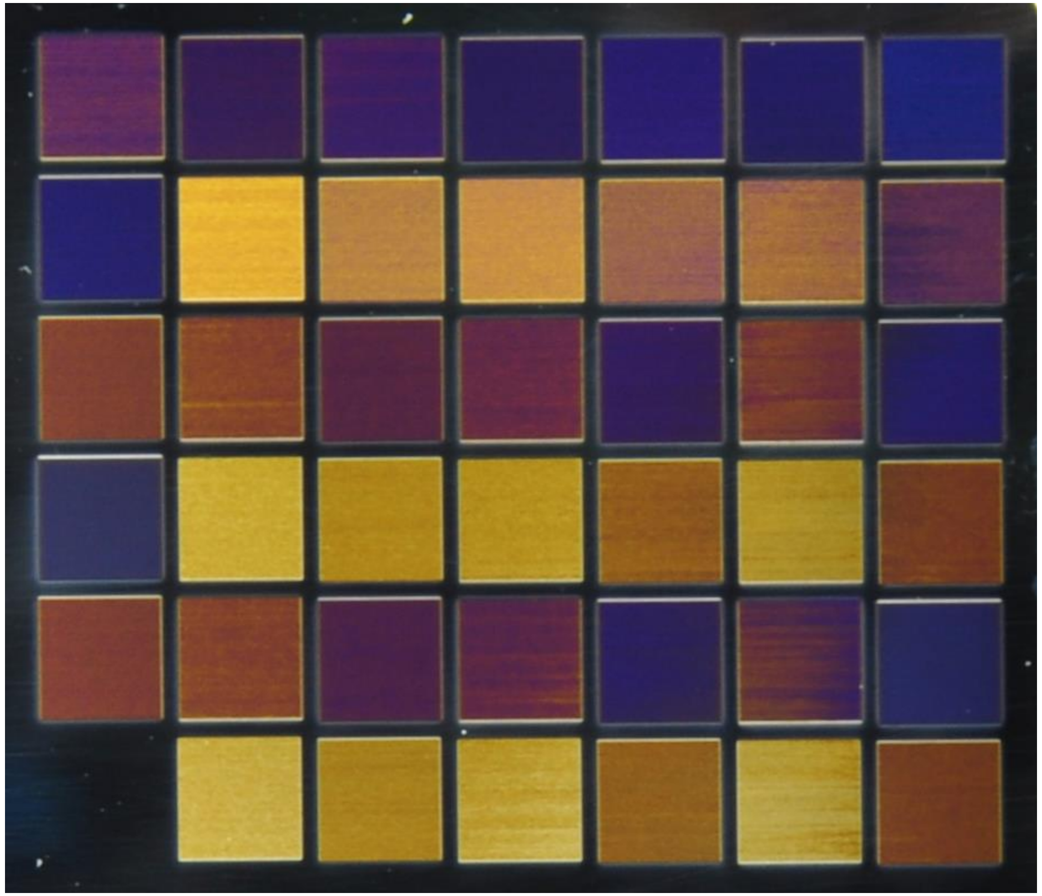
~1 Week later



Bulk Silver vs electroplated Silver on Brass

Bulk Silver sample

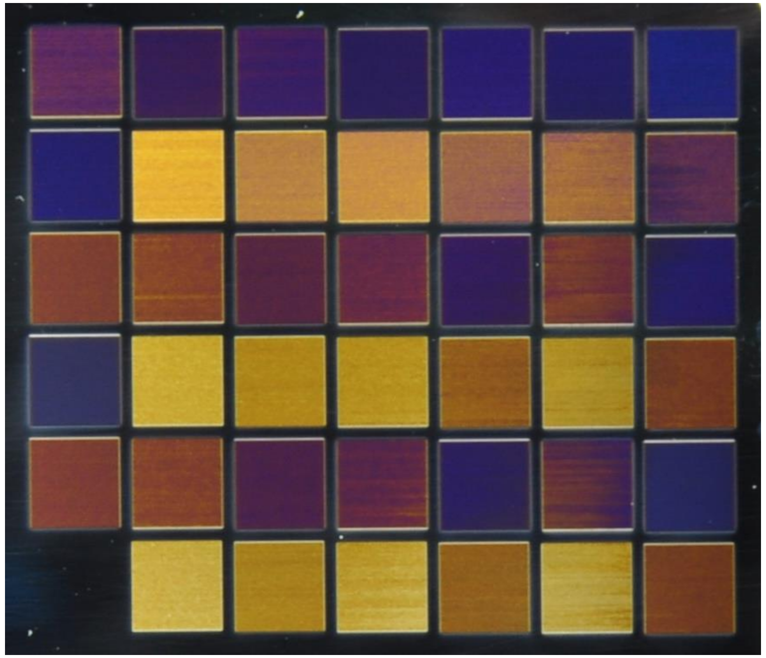
50µm electroplated Silver on Brass



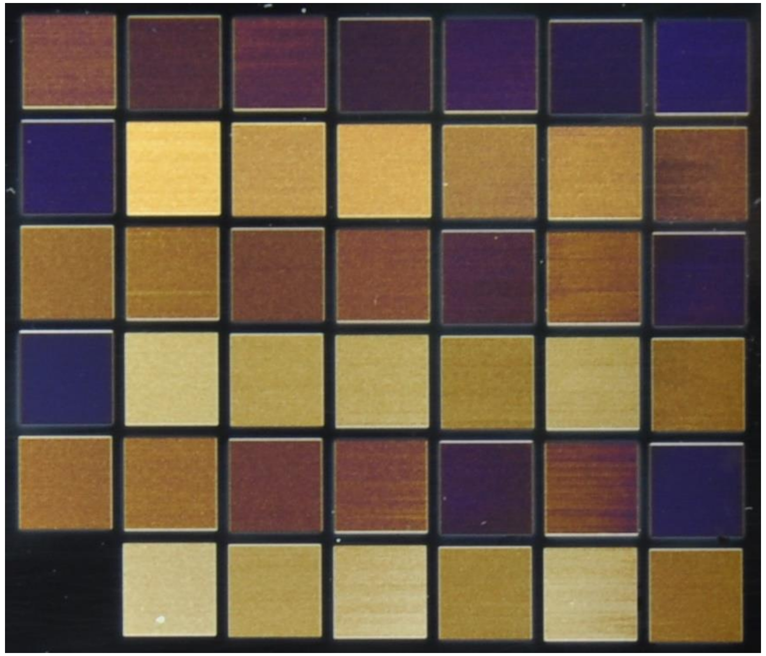
Conclusion: Same Process → Surface quality influences color

Degradation of Electroplated Ag

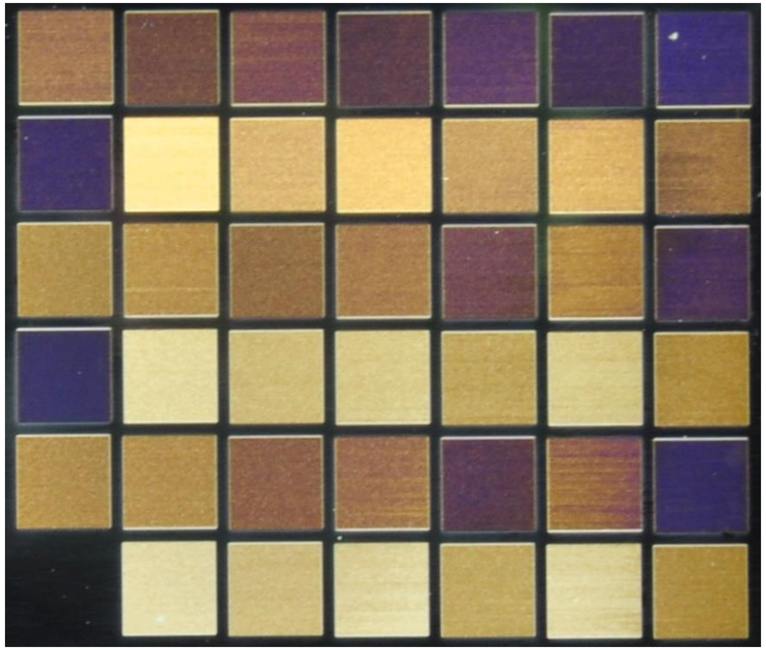
Sample after Processing



1 Week later



2 Weeks later



Conclusion: Same Process → Surface quality influences color degradation

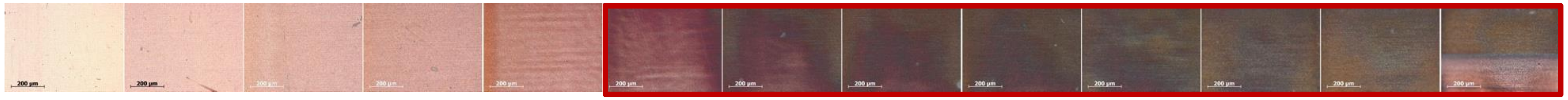
Color palette extension

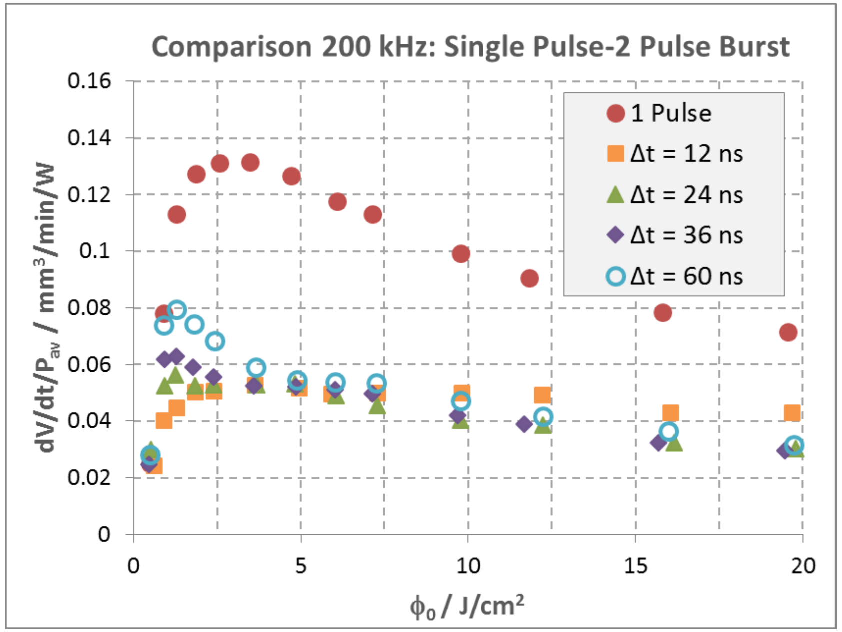
- Colors achieved solely through p_y variation by 0.25µm
- Small change in pulse overlap changes color significantly
- Colors remain stable after 70° ALD coating

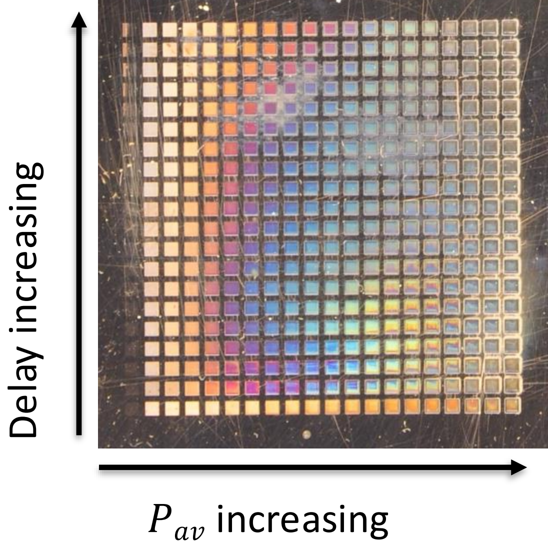
Parameters

- p_x =8µm
- P_{av} = 0.484W
- N_{Layer} =5
- f_{rep} = 50kHz
- n_{burst} = 3

Copper: 2 Pulse Burst



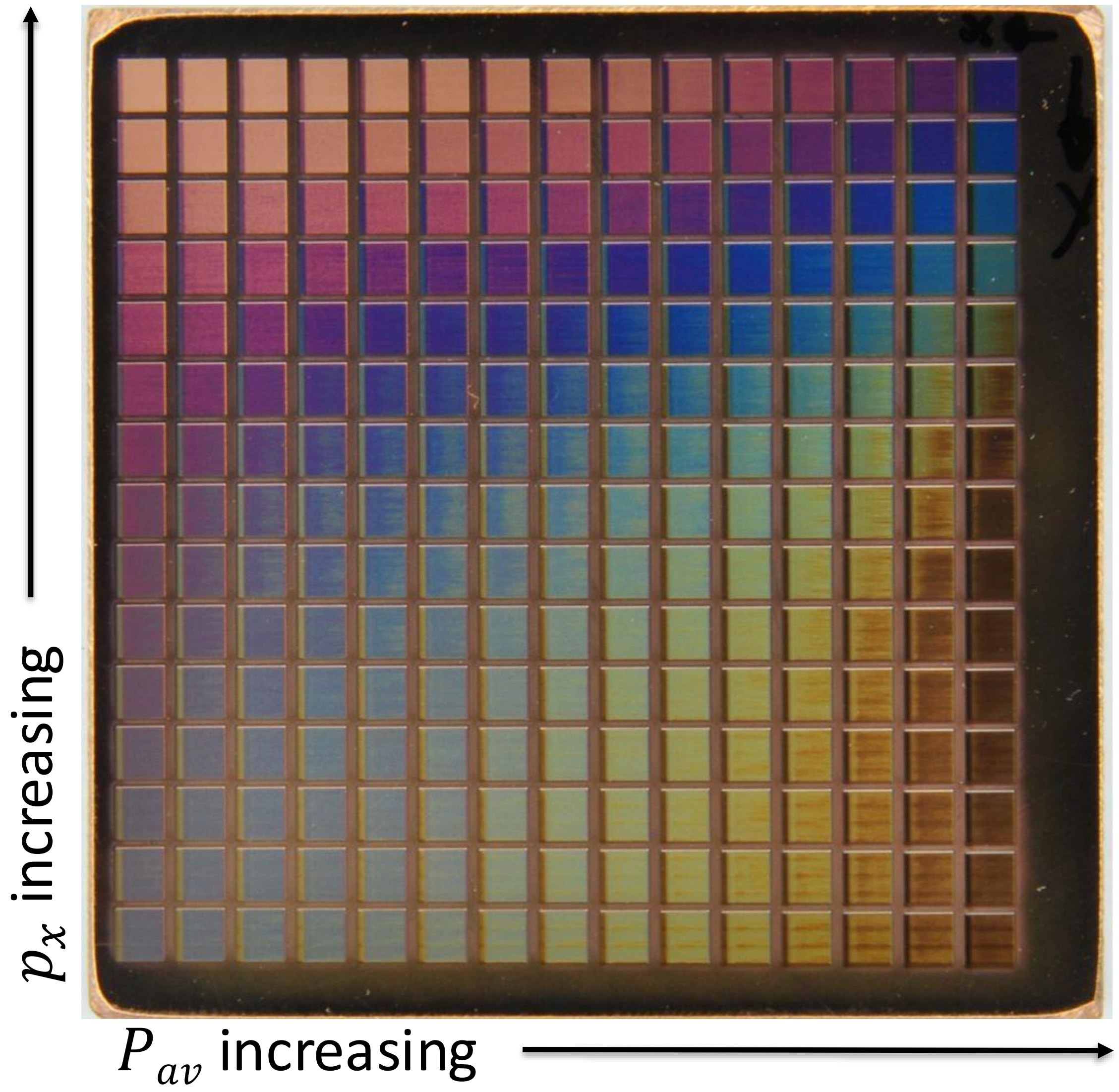




- f_r = 200kHz, w_0 = 16 µm
- Dramatic drop in the specific removal rate for 2 pulse burst
  -> Plasma shielding?
- Strong thermal coloring
- Increasing time separation does not lead to single pulse behavior

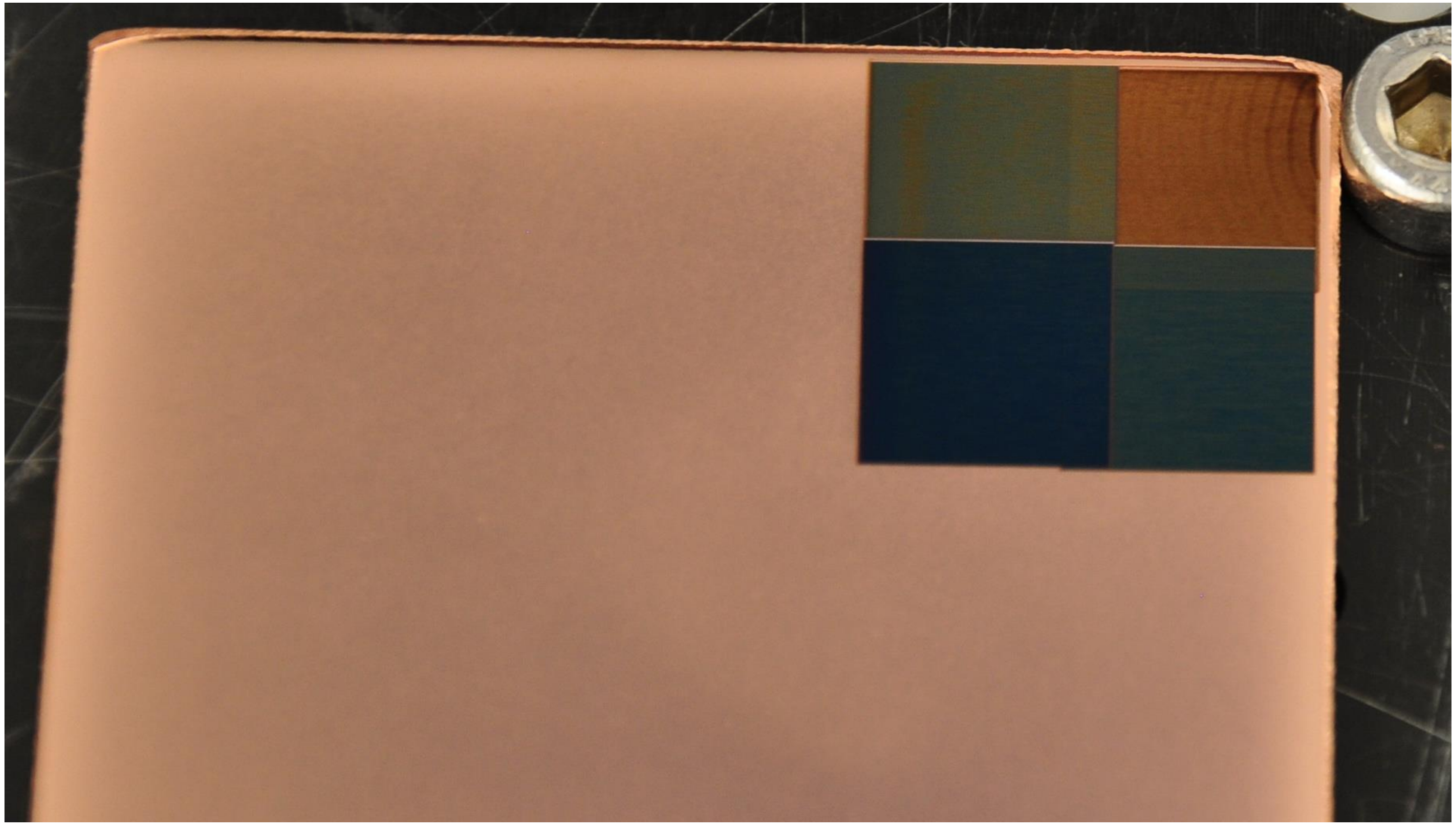
Variation of Fluence and Pitch on Copper

- Double pulses with 25 ns pulse separation provide bright colors
- Small variation in pitch and power provides rich color palette
- Only one layer needed
- Color formation remains stable on copper



Which layer defines the final color ?

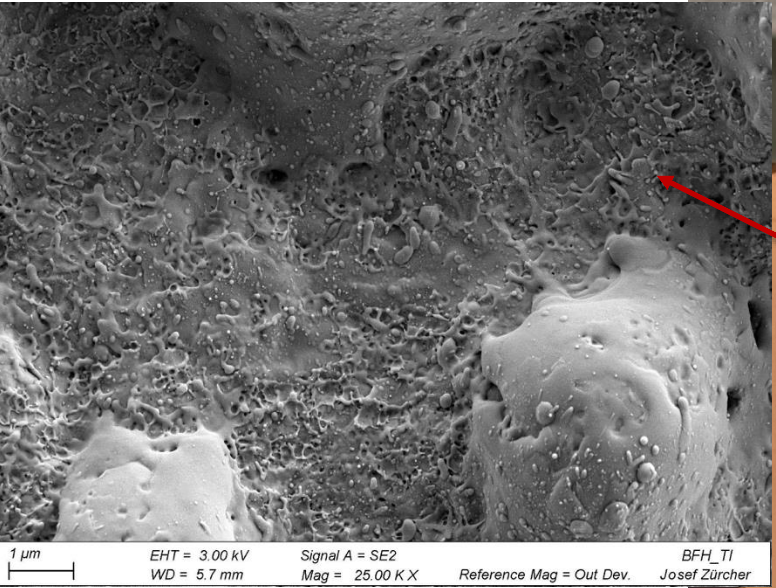
- Homogeneous colors on copper by 1 layer
- Differences in ablation depth don't influence final color
- **Last layer overrides previous color**



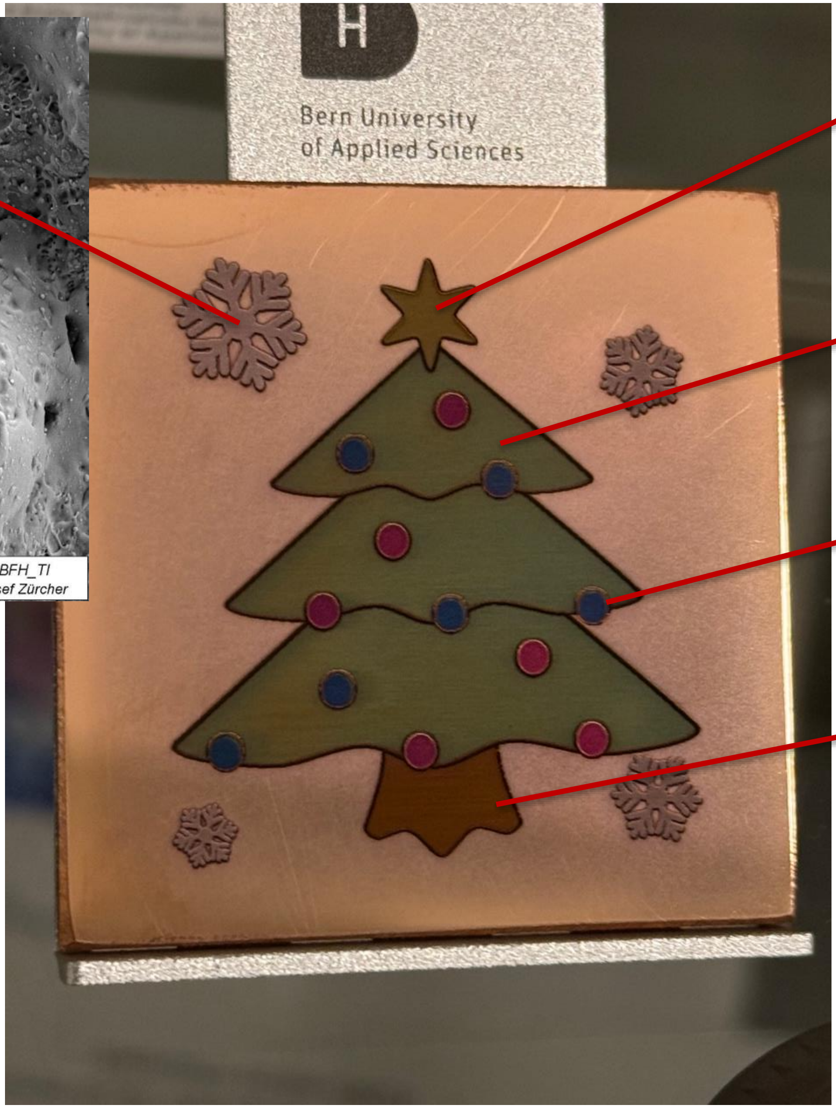
Parameters

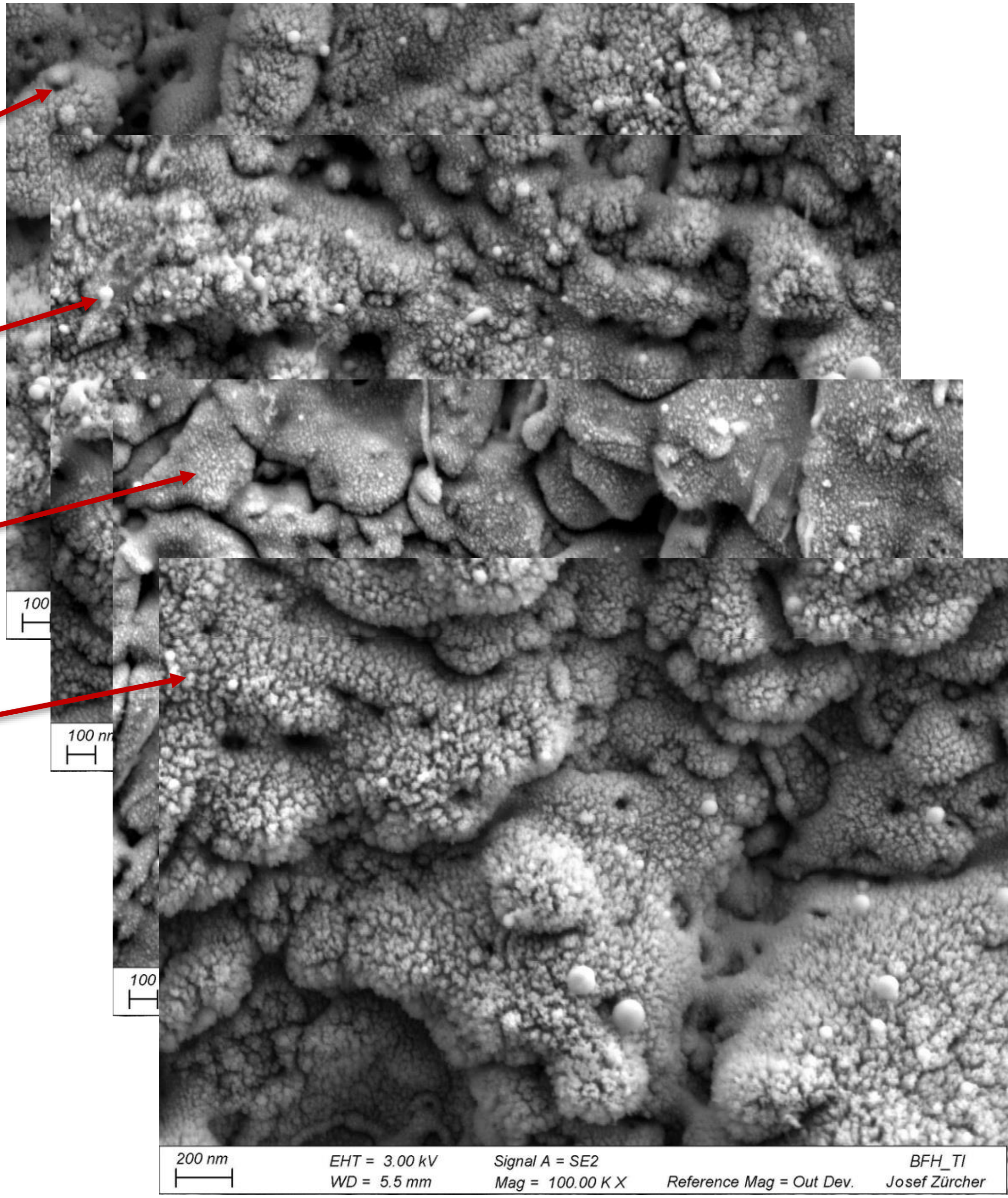
- $p_x = p_y = 8\mu m$
- P_{av} = 8.2W; 9.6W; 11.2W; 18.3W
- N_{Layer} = 1;2
- f_{rep} = 200kHz
- n_{burst} = 2

Christmas Tree demonstration and SEM Analysis



- NPs present on all colors except white
- Size distribution difficult to evaluate
- Differences in ablation depth don’t influence final color

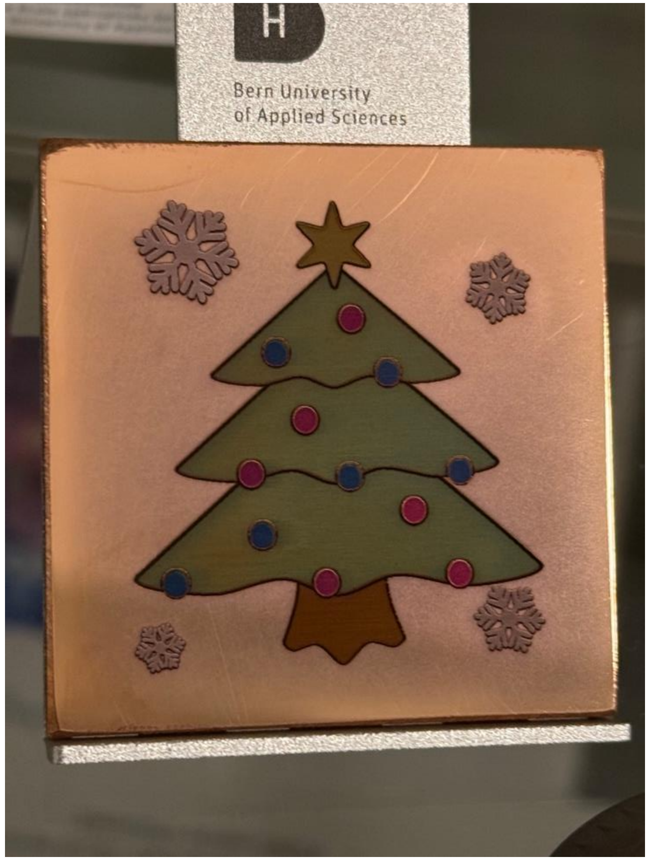




Conclusions and Lessons Learned

- Plasmonic colors are generated by a **sensitive interplay** of ablation, NP agglomeration in the plume, redeposition due to burst mode pulses and melt phase generation for embedding the NPs
- Small variation of pulse overlap changes color significantly
- Copper produces nice structural colors, which don't change with time
- ALD layer important for color preservation and scratch resistance

Thank you for your attention



LinkedIn video QR code

For further information please contact: rainer.kling@bfh.ch

https://www.linkedin.com/posts/beat-neuenschwander-b9b98b23_laser-induced-plasmonic-colors-on-copper-activity-7274732597660839936-YJwC?utm_source=share&utm_medium=member_ios