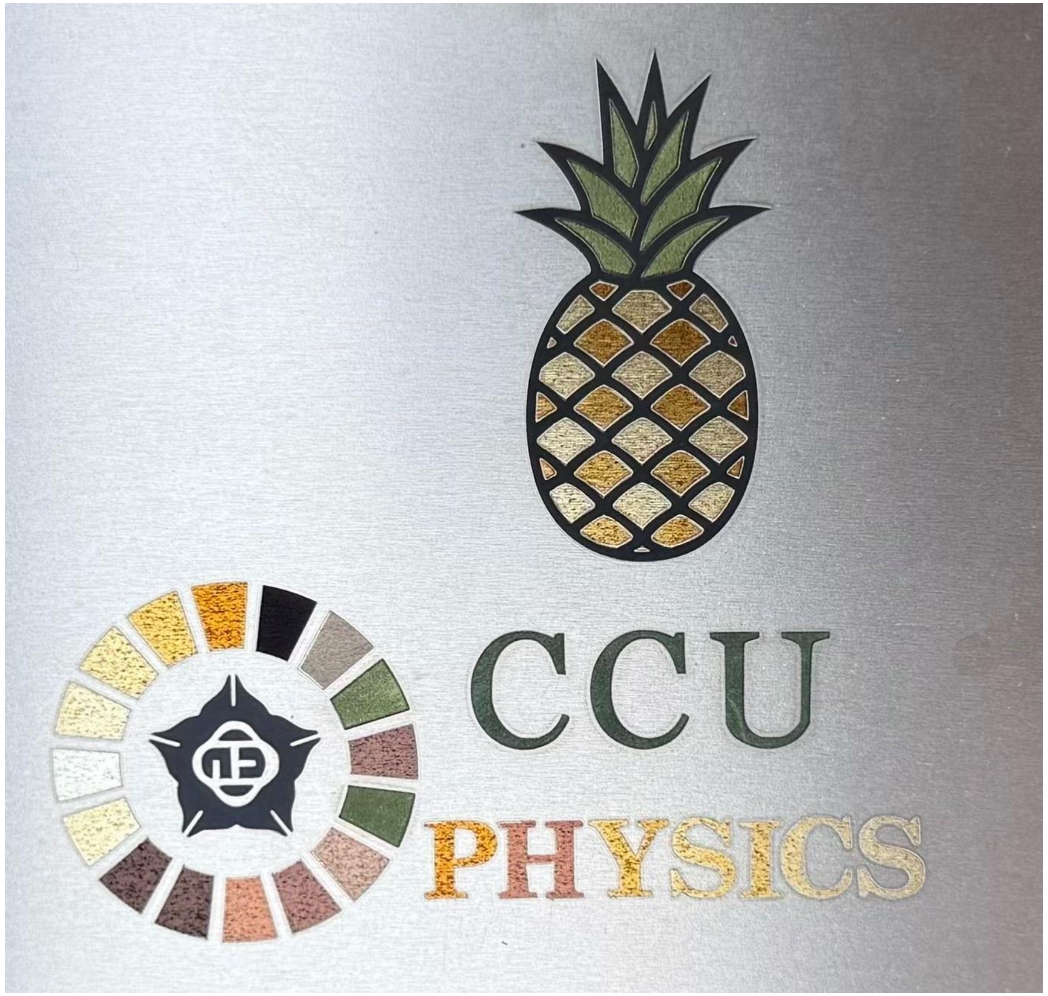
Laser Coloring on Titanium Plate

Member: 鄭睿哲　廖珈揚　林孟澤

Department of Physics,
National Chung–Cheng University
Advisor: 姚松偉

Phenomenon

Laser engraving can induce distinct colorations on titanium and stainless-steel surfaces, with the resulting colors strongly dependent on processing parameters such as pulse width, pulse energy, scanning speed, and laser wavelength.



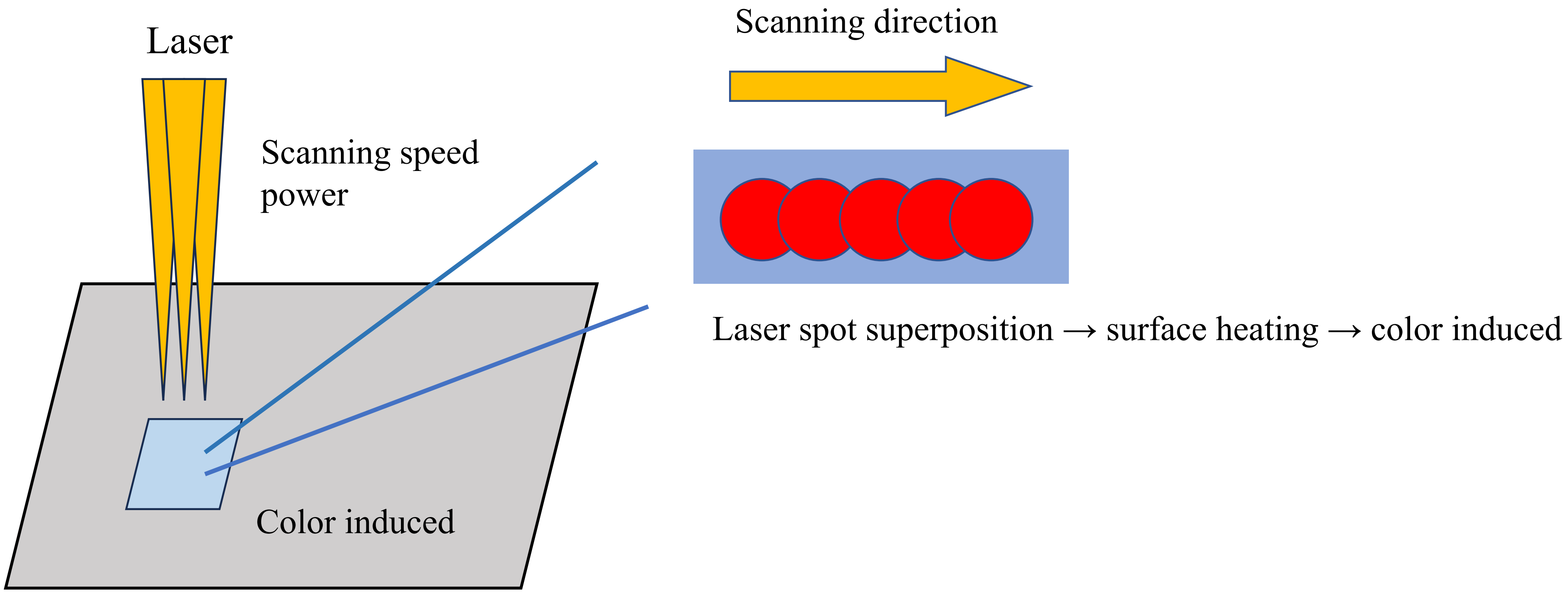
Objectives

- Color Gamut of Laser Processing
- Effect of Pulse Energy on Color
- Effect of Scanning Speed on Color
- Underlying Coloring Mechanism

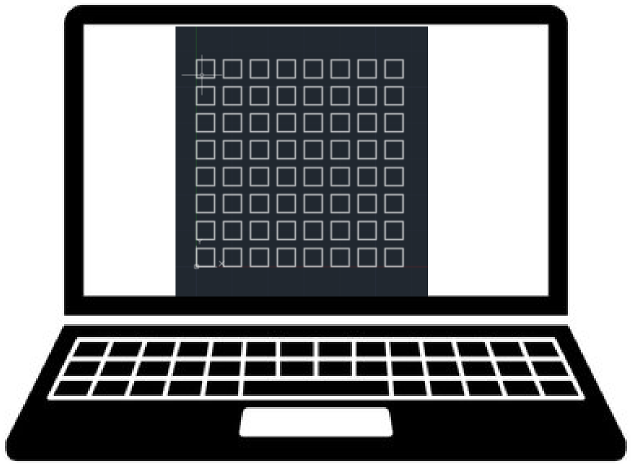
Outline

- Our approach
- Experimental setup
- Color Gamut in response to scanning parameter
- Coloring Mechanism
    - ➢Nano crystal → No
    - ➢Interference
- Propose mechanism
- Numerical simulation (Peak temperature → thickness of oxide layer)
- Spectral analysis
- Conclusion & Outlook
- Appendix
    - ➢Light source selection
    - ➢Theories
    - ➢CIE 1931

Our approach

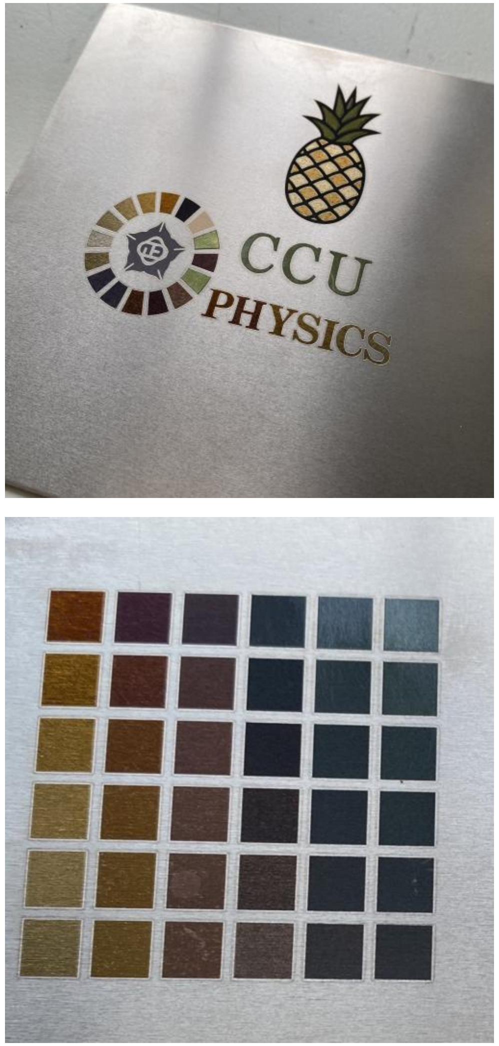


Experimental setup and methods



1. AutoCAD design
2. Scanning parameters

Laser engraver
(台灣三軸, TLS400-30W-P3)



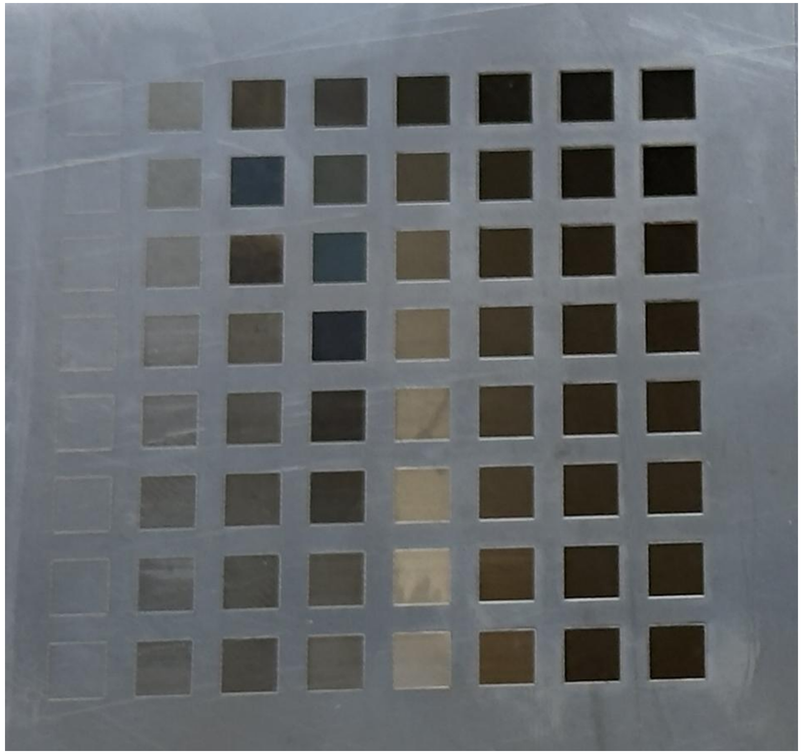
Results

Average laser power [W]	3 – 12	Major parameter
Scanning speed (mm/s)	50-275	Major parameter
Pulse repetition rate (kHz)	30	Fix parameter (tool dependence)

Color Gamut

Titanium

Stainless steel 304

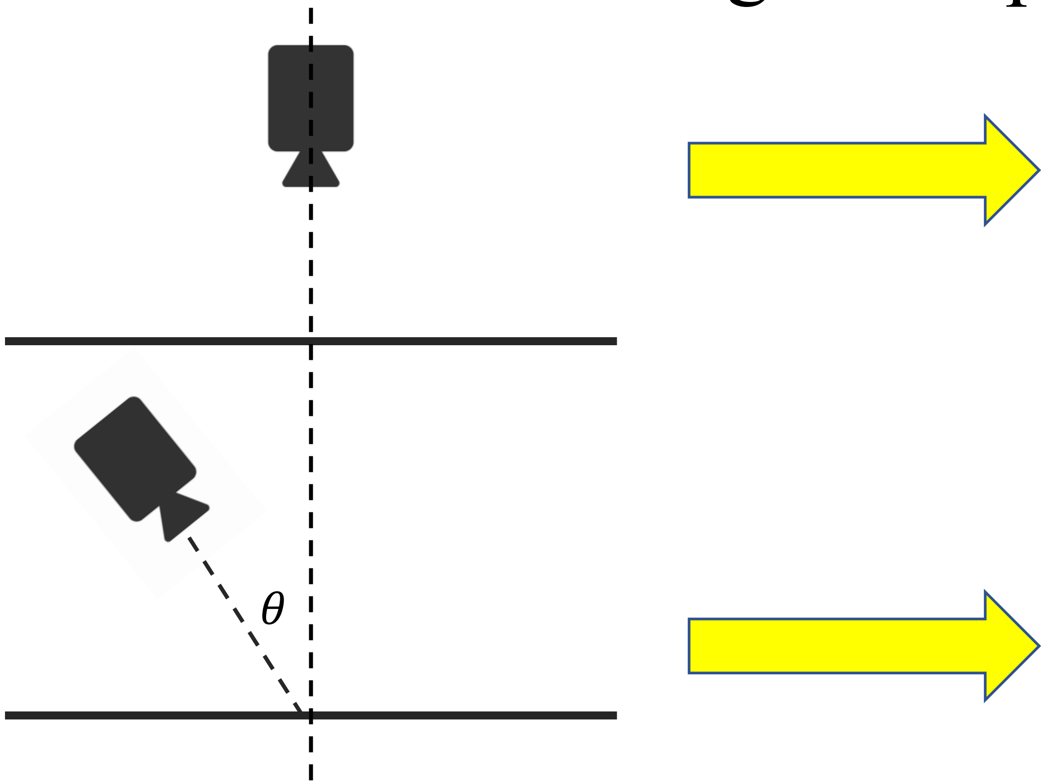


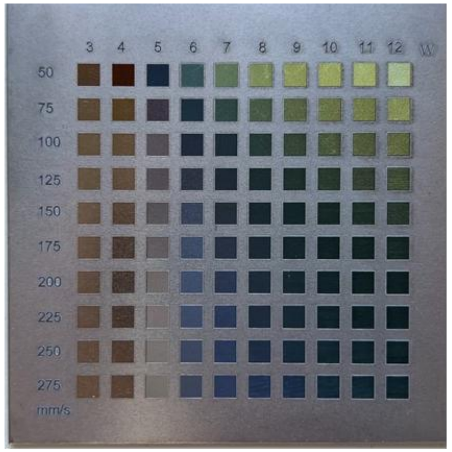
Stainless steel with very limited color Gamut
→ Focus on titanium plate in the following discussion

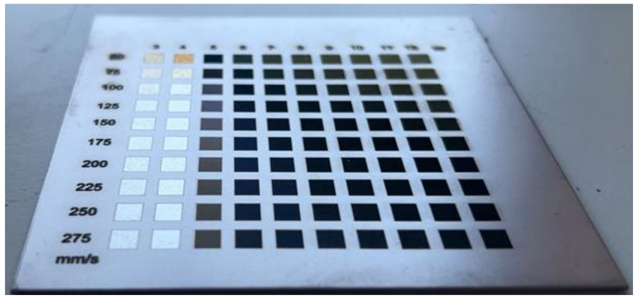
Coloring Mechanism

Viewing angle dependent coloring

- Nano-crystal coloring → excluded
- Interference coloring → suspected







Coloring Mechanism

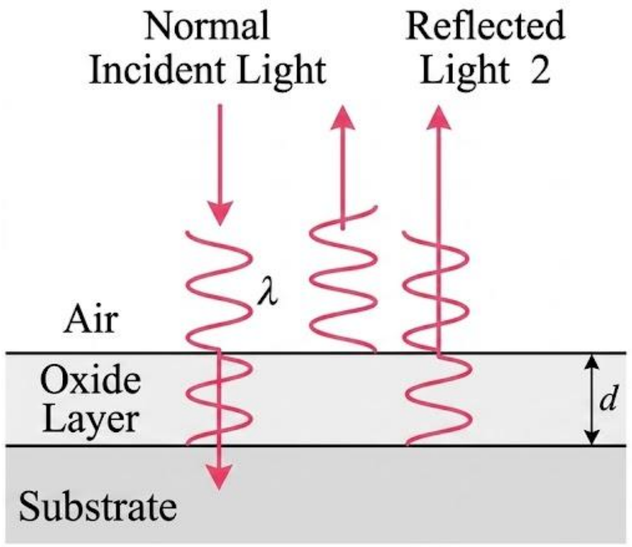
• Thin-film Interference

Optical Path Difference (光程差): Incident light is reflected at the surface of the oxide layer, while part of the light is refracted into the thin film and reflected back from the metal substrate. These two light waves produce a phase difference, causing constructive interference or destructive interference (reduction) at specific wavelengths.

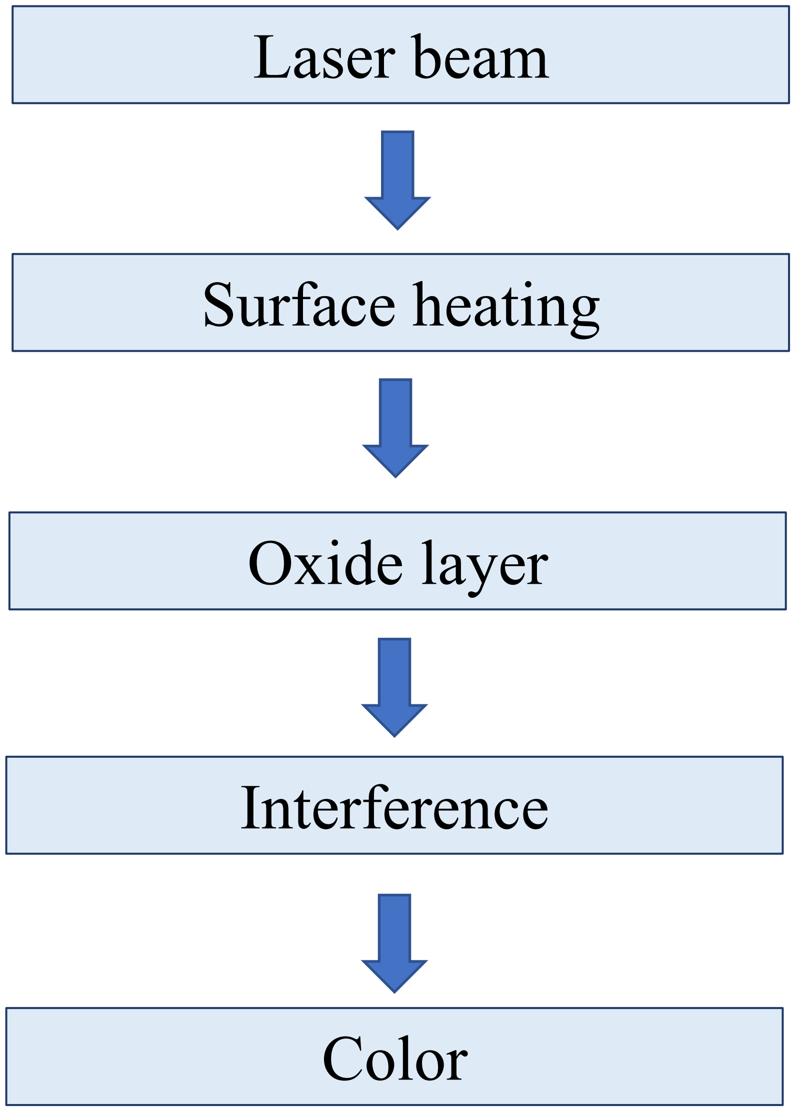
Constructive interference:

$$2nd + \triangle\varphi = m\lambda$$

- d:the thickness of oxide layers
- n:Refractive Index
- φ:Phase Correction
- m:Interference Order
- $m\lambda$:Target Wavelength



Proposed Mechanism



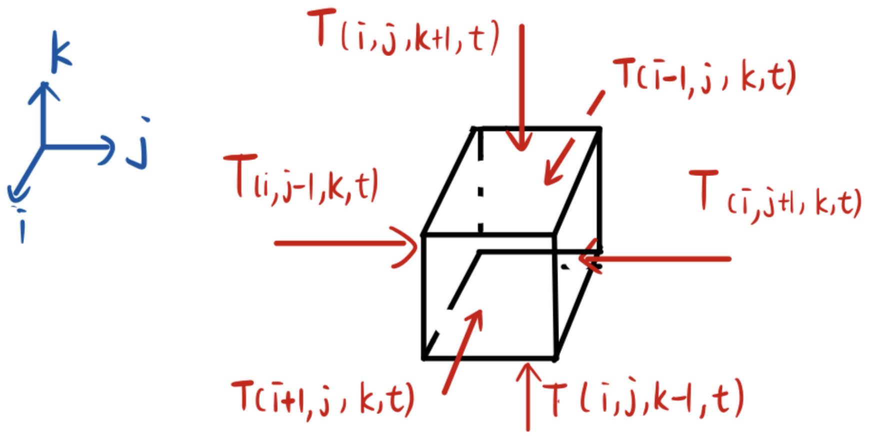
Numerical simulation (surface peak temperature)

Fourier Law:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q$$

C_p: heat capacity
k: heat conductivity
Q(x,y; t): heat source (laser pulse)

Numerical grid:

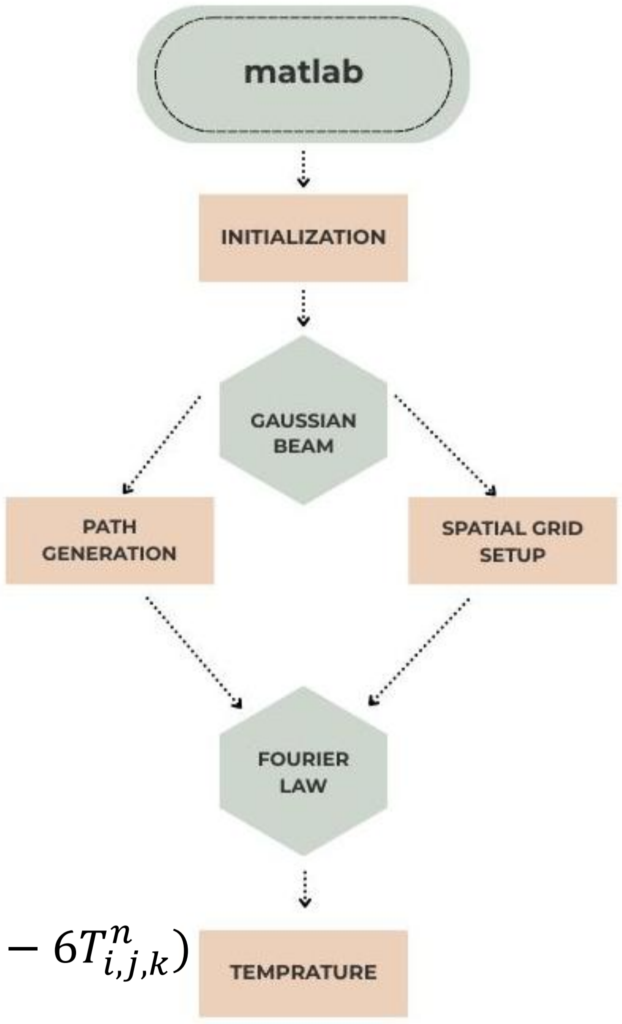


$$\frac{\partial^2 T}{\partial x^2} = \frac{T^n_{i+1,j,k} + T^n_{i-1,j,k} - 2T^n_{i,j,k}}{\triangle x^2}$$

$$\nabla^2 T = (\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2})$$

$$\frac{\partial T}{\partial t} \cong \frac{T^{n+1}_{i,j,k} - T^n_{i,j,k}}{\triangle t}$$

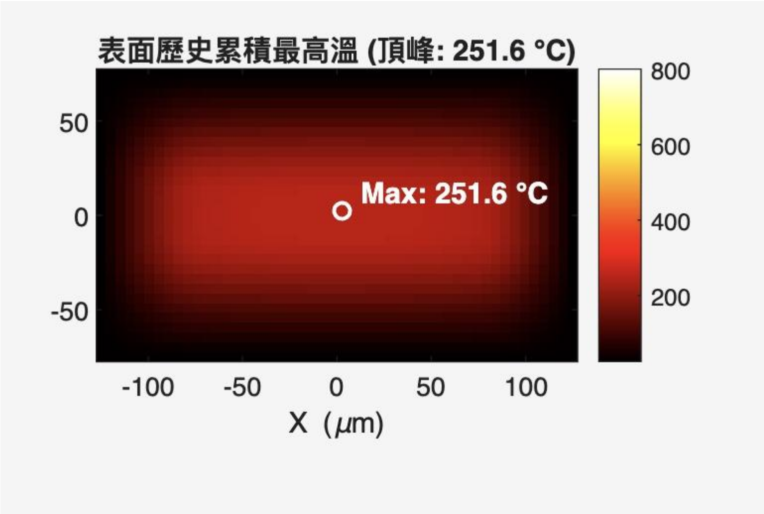
$$T^{n+1}_{i,j,k} = T^n_{i,j,k} + (\frac{k \triangle t}{\rho C_\rho d^2})(\Sigma T_{neighbors} - 6T^n_{i,j,k})$$



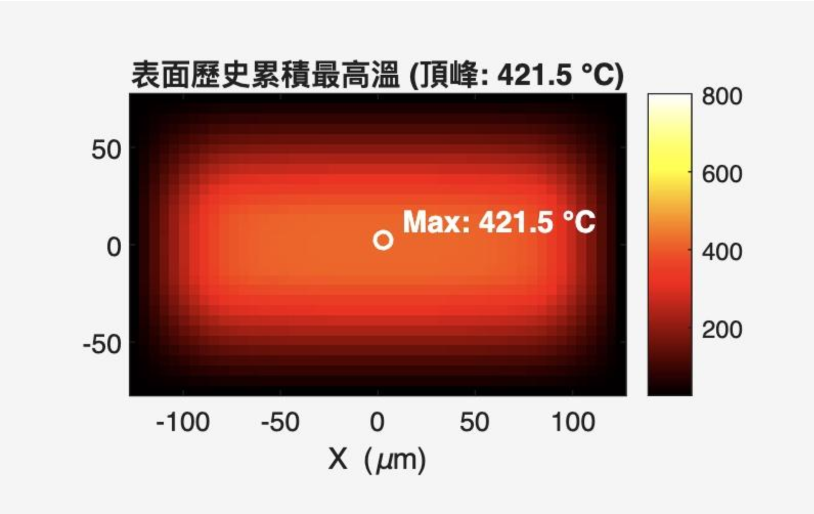
Numerical simulation (surface peak temperature)

Effect of Laser Power on Oxide Thickness (Constant Speed)

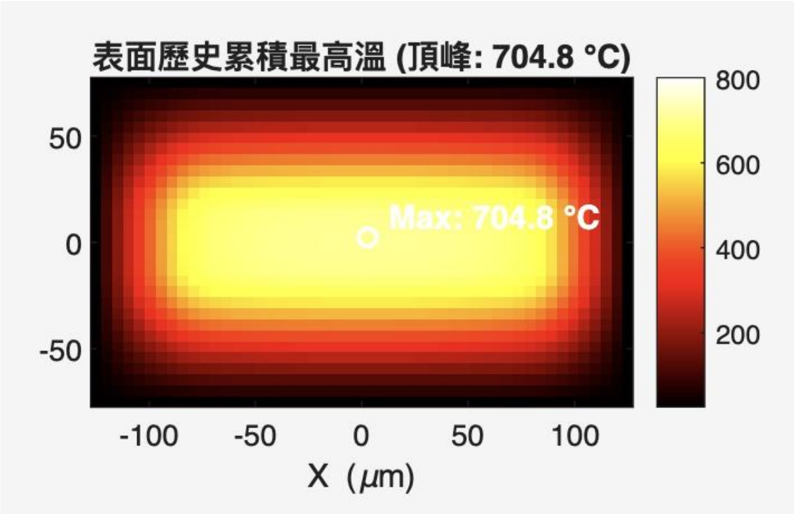
P=4w



P=7w

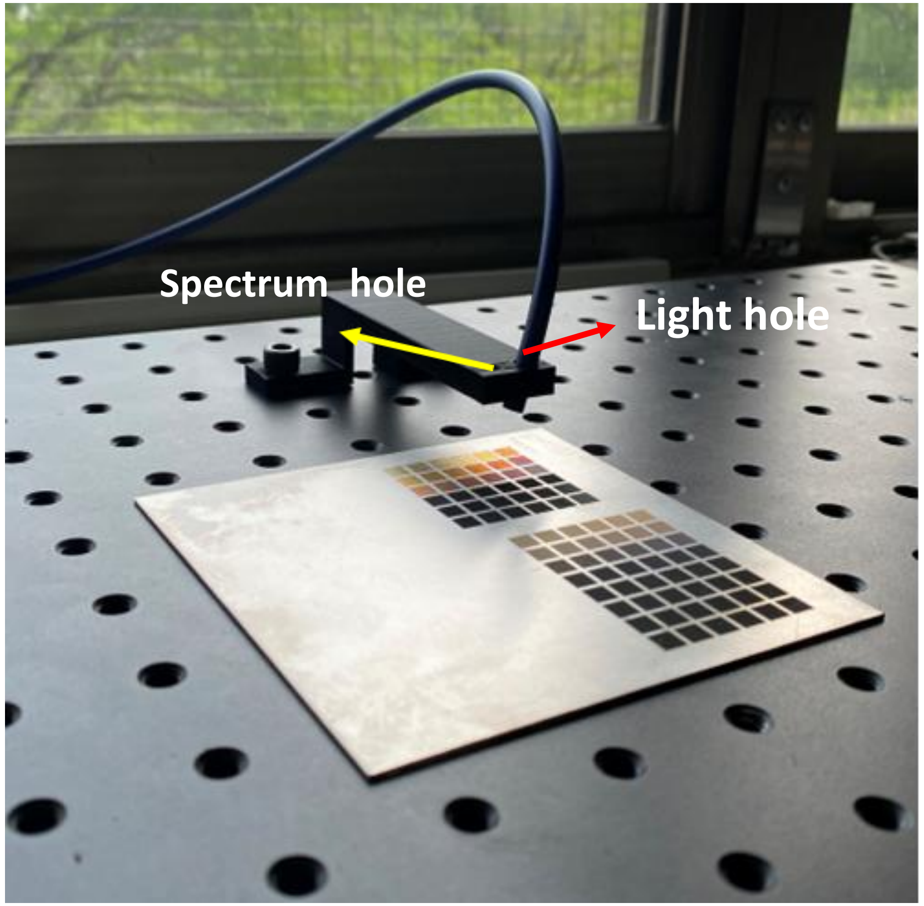


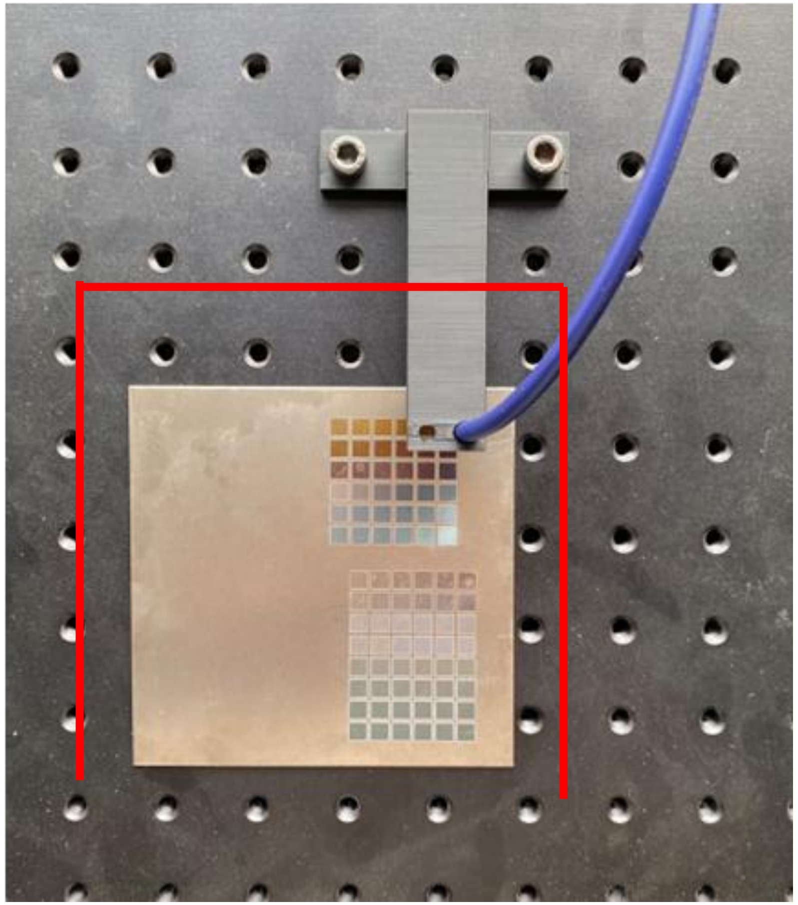
P=12w



Spectral analysis

Using two different light sources to analyze*

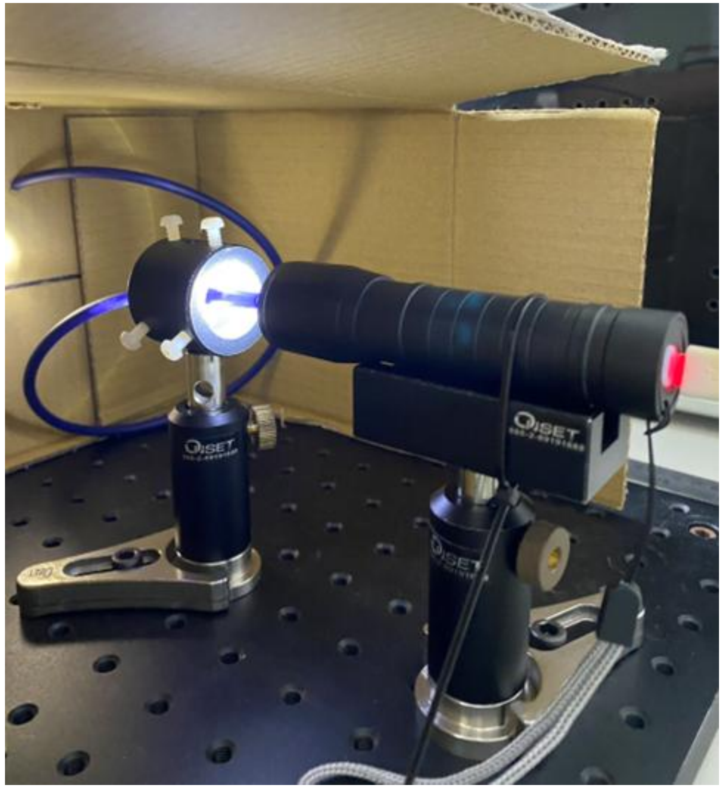


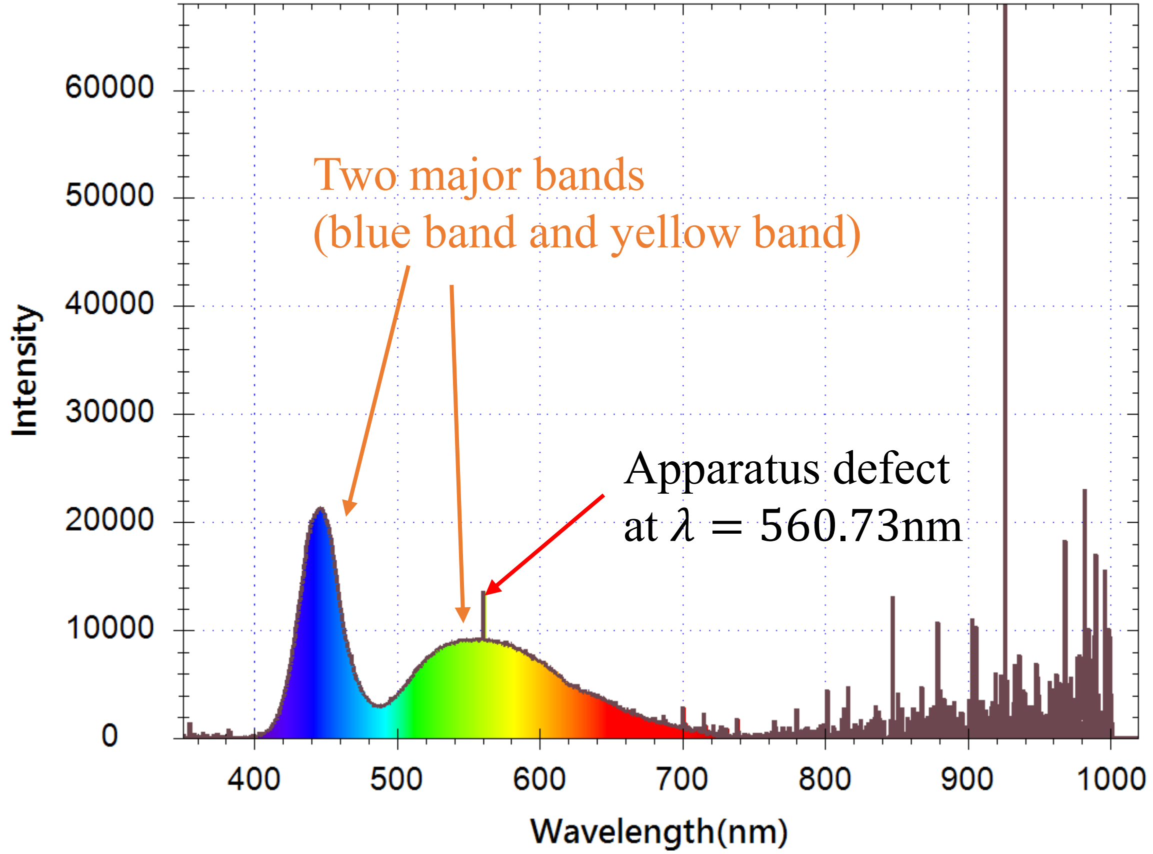


*For detailed explanation, see appendix.

Spectral analysis

Method : LED as light source



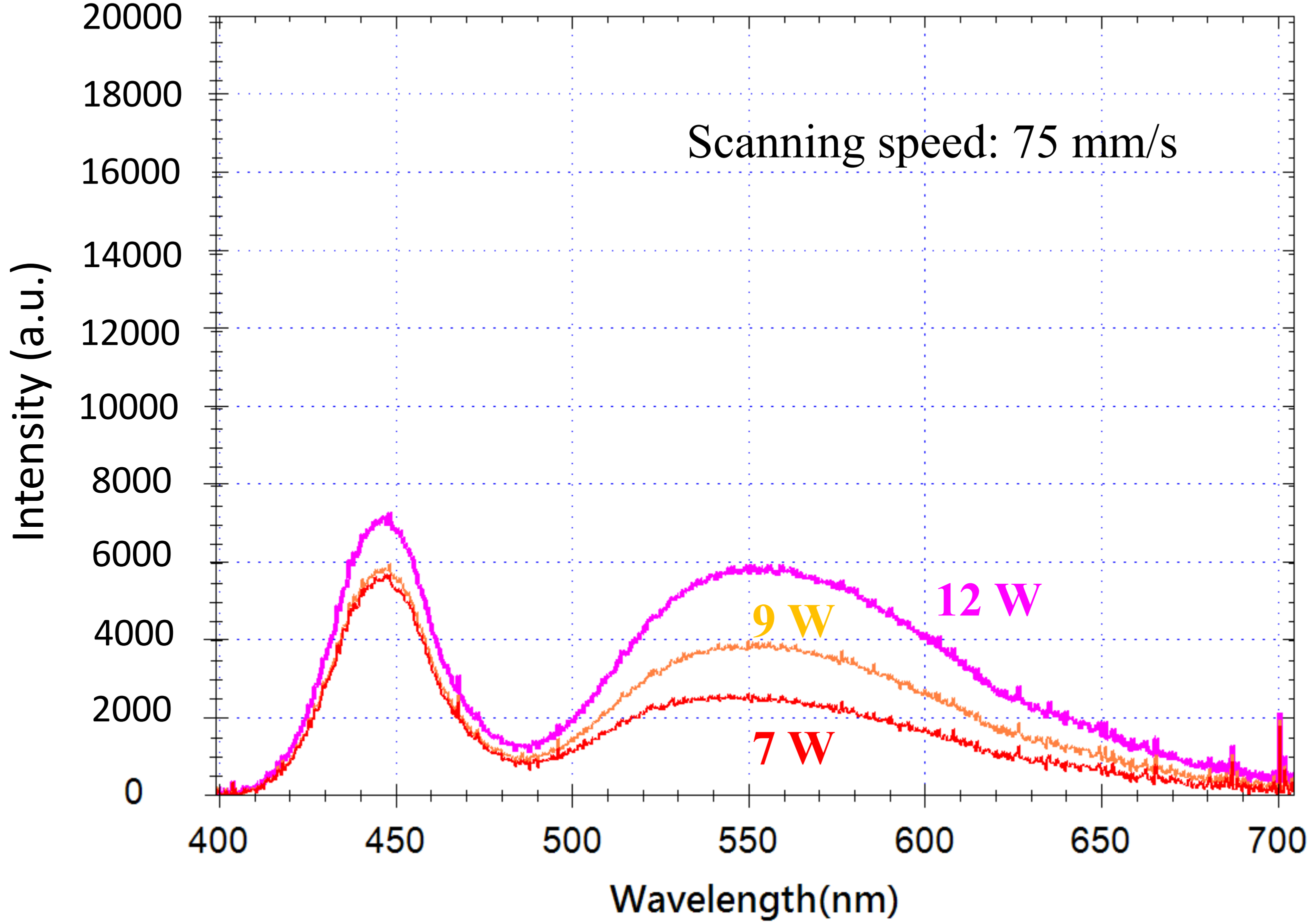


During the visible section have better behavior. Large intensity.

Spectral analysis

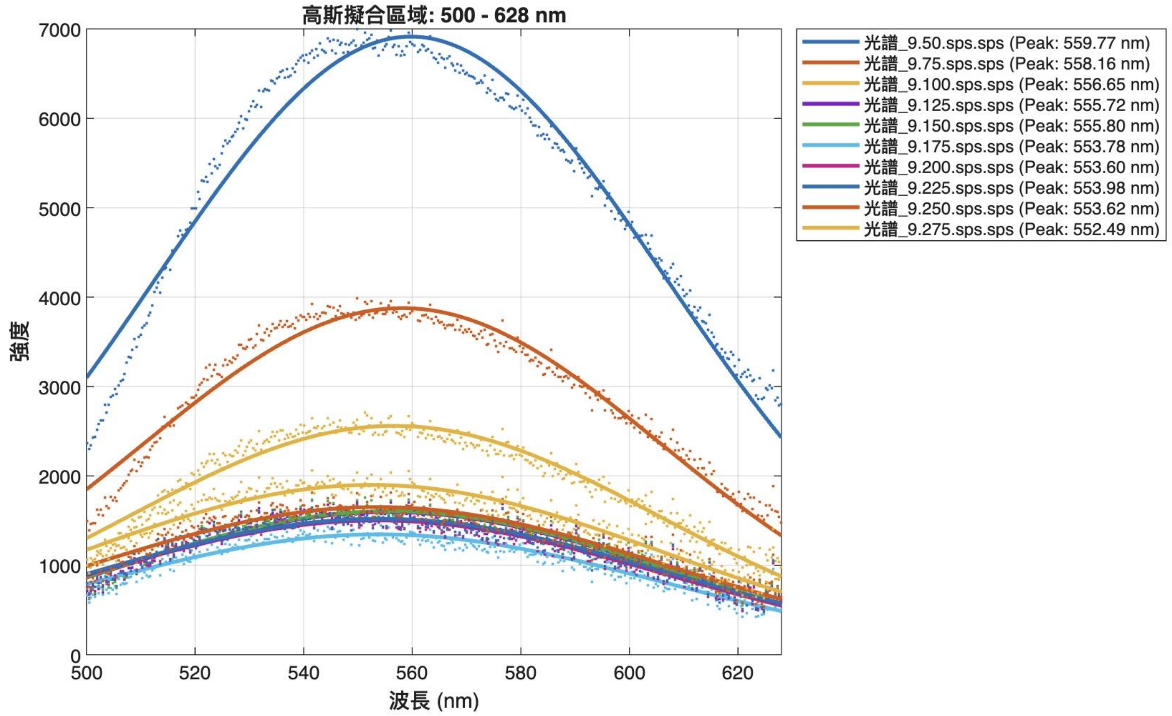
Analysis of actual samples under test (from 100 data with obvious behavior)

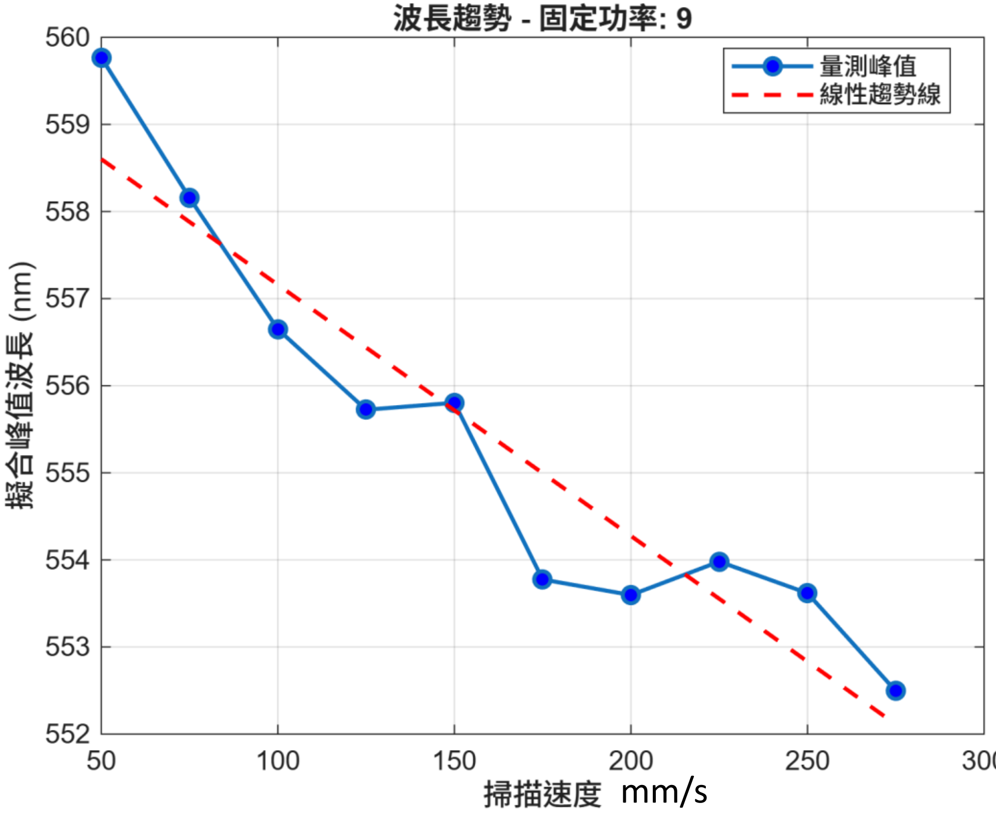
Choosing the 2nd row of 10×10 samples (1) 7w;75mm/s (2) 9w;75mm/s (3) 12w;75mm/s



Spectral analysis

Yellow region

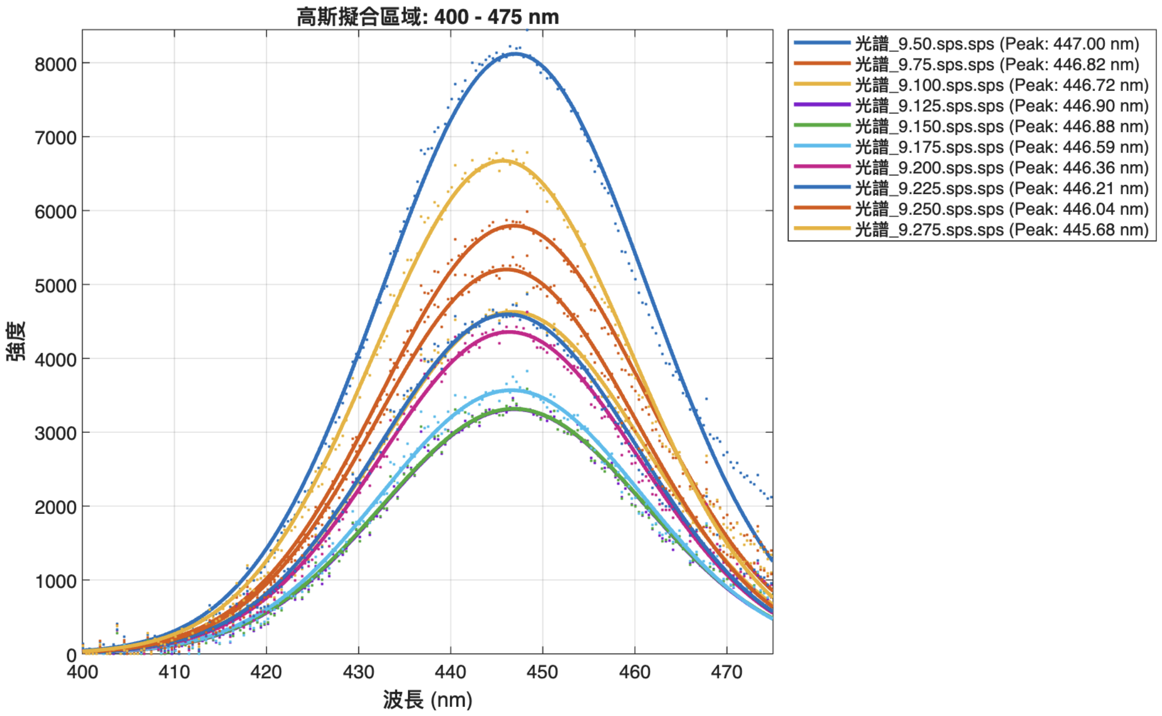


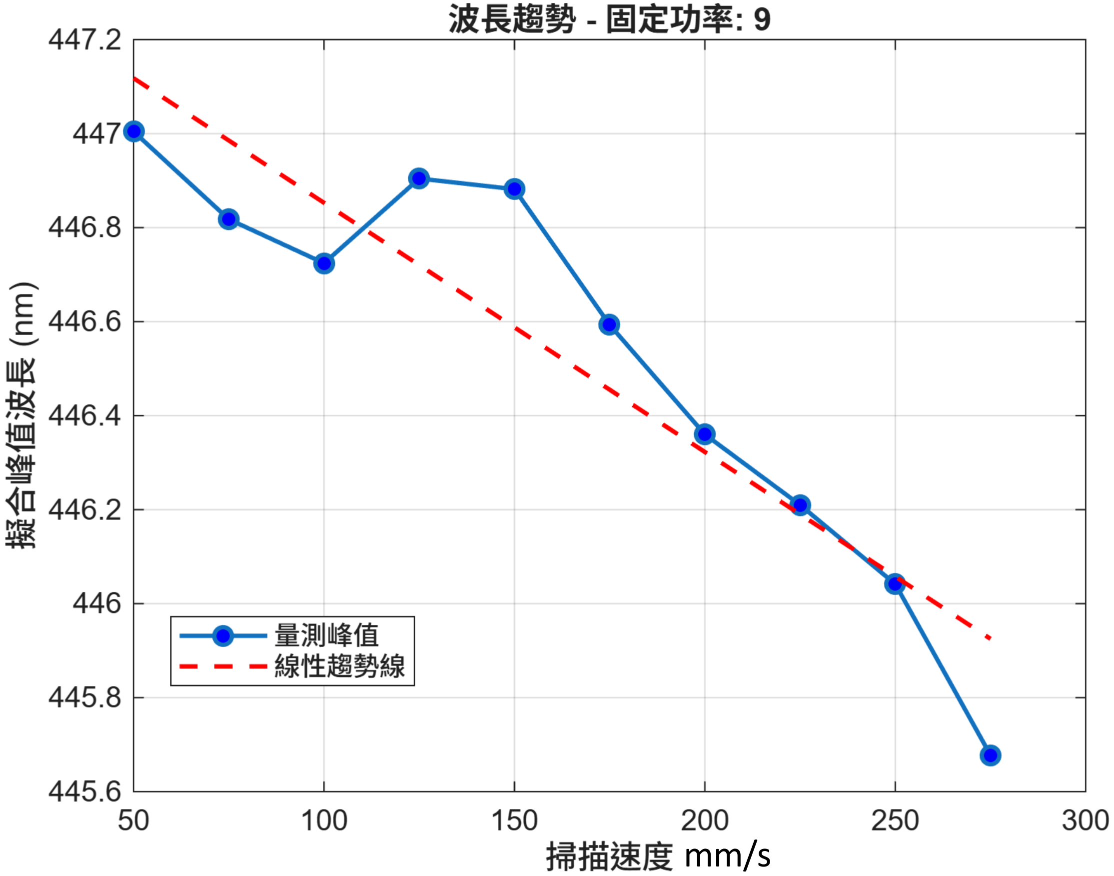


mm/s	50	75	100	125	150	175	200	225	250	275
°C	532.81°C	530.33°C	527.05°C	523.14°C	518.78°C	514.14°C	509.35°C	504.57°C	499.91°C	495.32°C

Spectral analysis

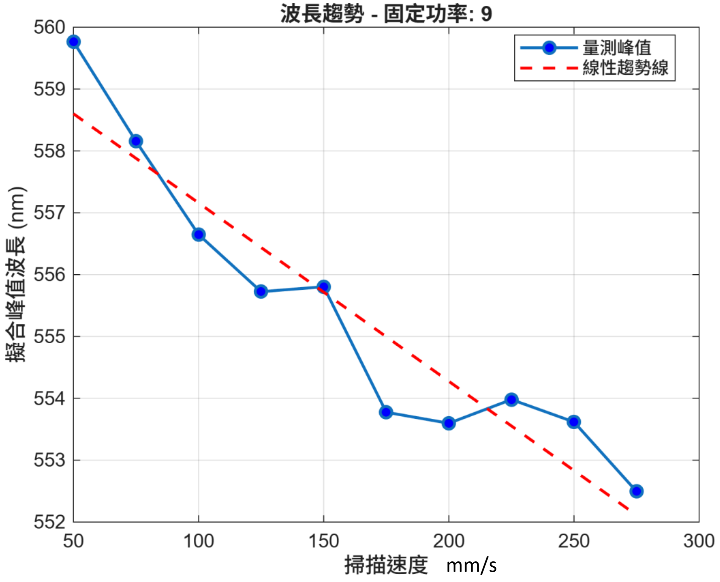
Blue region

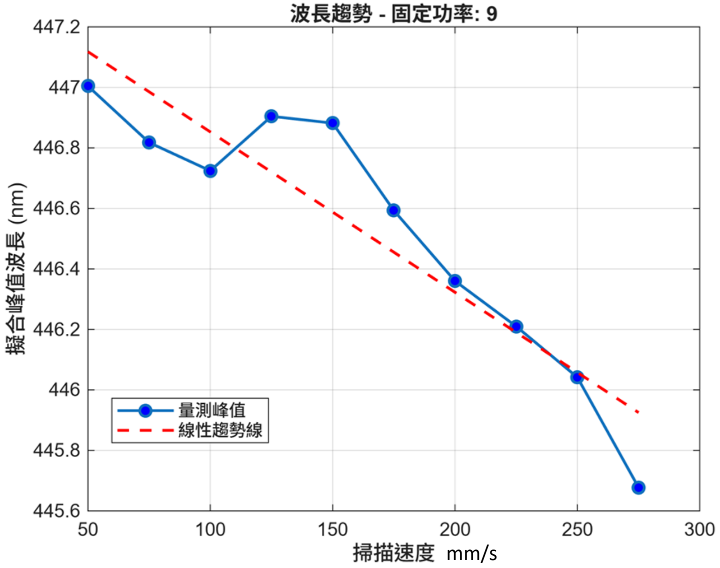




mm/s	50	75	100	125	150	175	200	225	250	275
℃	532.81°C	530.33°C	527.05°C	523.14°C	518.78°C	514.14°C	509.35°C	504.57°C	499.91°C	495.32°C

Spectral analysis





Fixed power: 9w

As scanning speed increase, the laser fluence (雷射能量密度) **decrease**, causing the thickness of oxidation ***d*** **decrease** as well.

Meanwhile, the interference equation gives

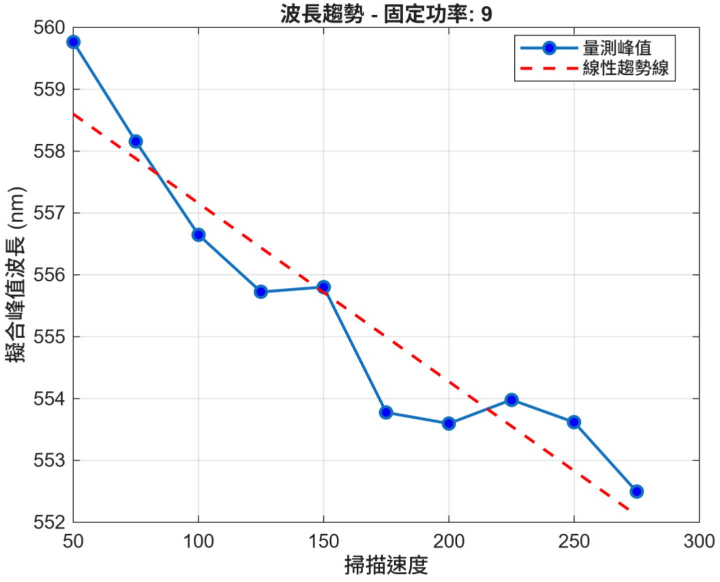
$$2nd = m\lambda$$

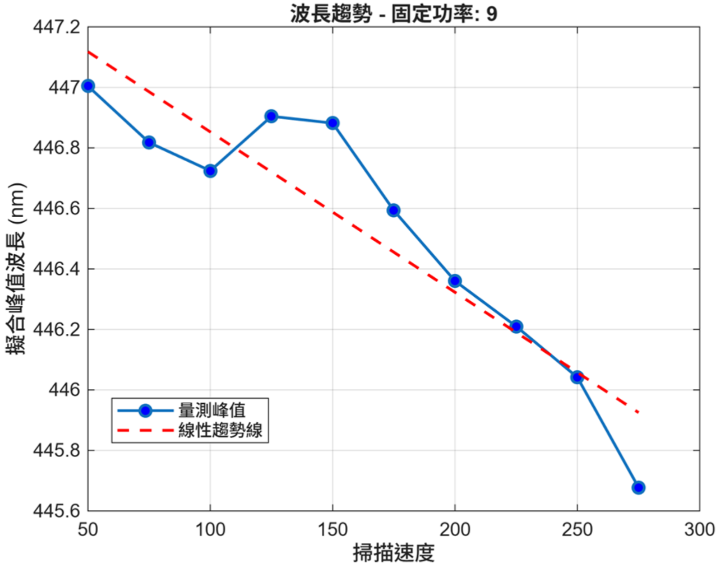
therefore,

$$d\downarrow;\ \lambda\downarrow$$

clearly showing that the TiO2 thickness exhibits an approximately linear dependence on the deposited laser fluence.

Spectral analysis





The swing curve.

$$2nd = m\lambda$$

As the scanning speed increases, the thickness ***d*** changes continuously.

However, the interference condition cycles (循環) between constructive and destructive interference.

Order transition (m):

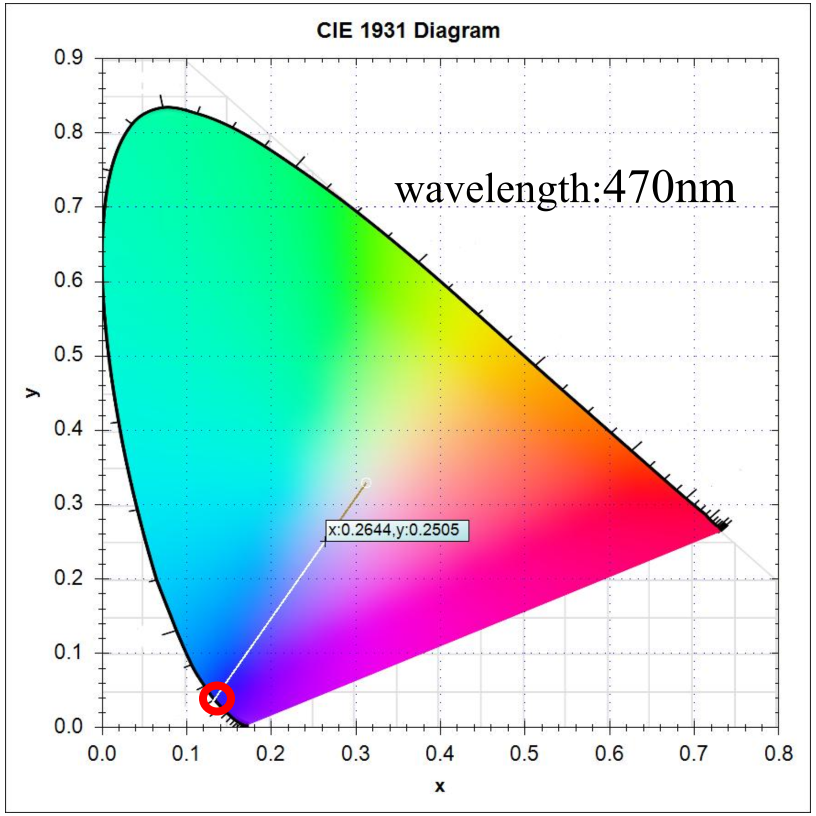
Thickness crosses a multiple of $\lambda/2n$,
the interference enters the next cycle (m→m+1), causing a “turning point” or jump in the data curve.
當厚度越過臨界值，原本的主峰強度可能減弱，而旁邊的次峰（下一階）強度增加。

The swing curve is the behavior of spectral features (光譜特徵) as they pass through different interference cycles.

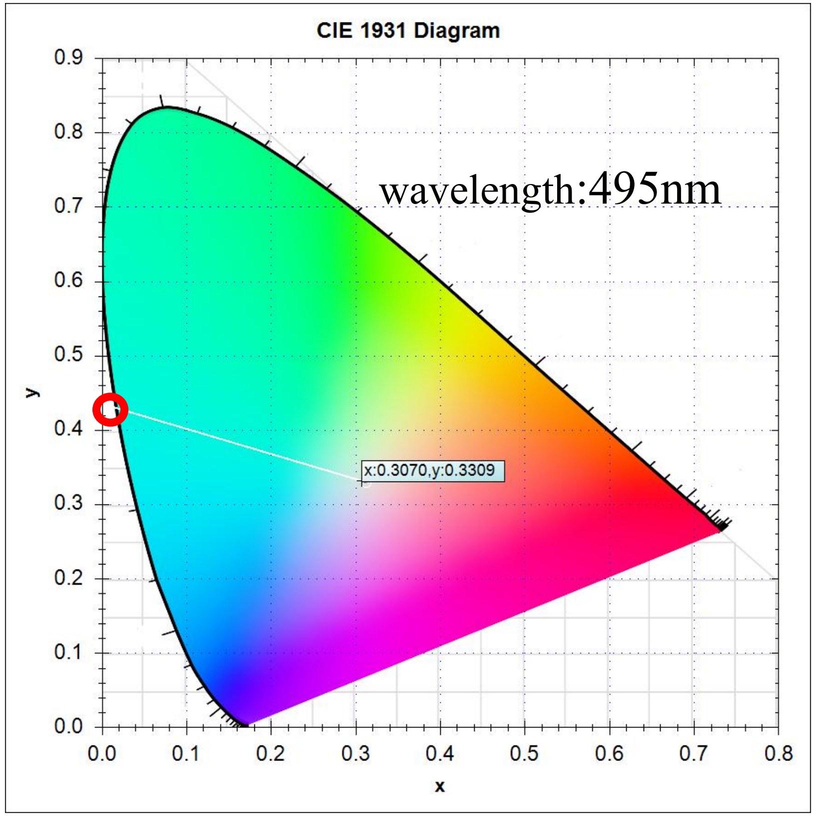
Spectral analysis

Analysis of actual samples under test (from 100 data with obvious behavior)

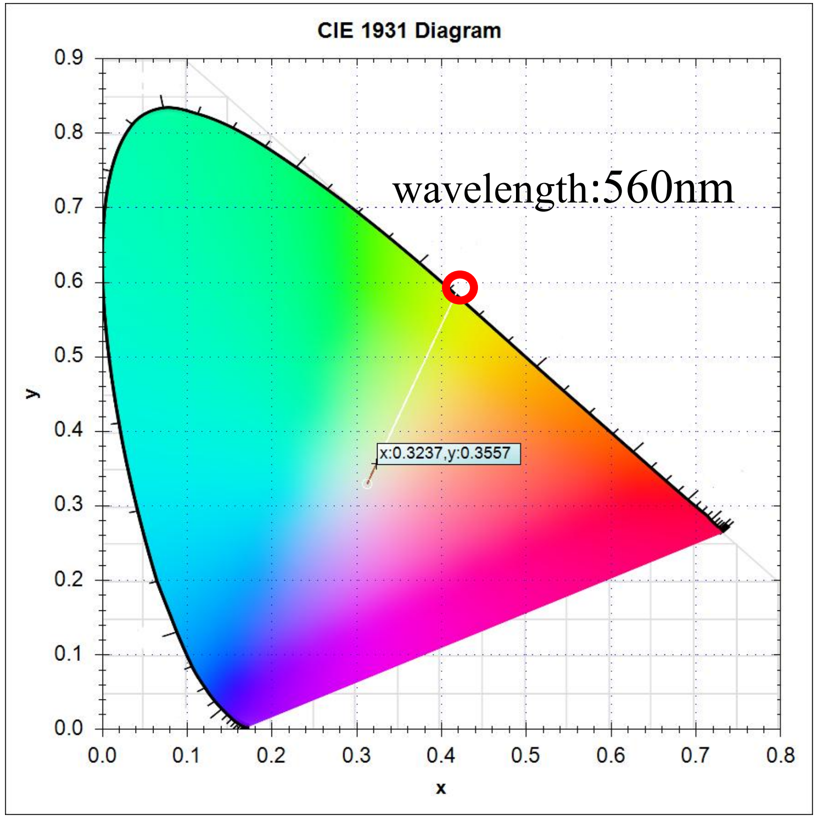
Choosing the 2nd row of 10×10 samples (1) 6w;75mm/s (2) 9w;75mm/s (3) 12w;75mm/s



6w;75mm/s



9w;75mm/s



12w;75mm/s

Spectral analysis

V=75mm/s

10	(0.3193, 0.348	主波長	555 nm
11	(0.3222, 0.352	主波長	560 nm
12	(0.3237, 0.355	主波長	562 nm

Green region

V=175mm/s

6	(0.2702, 0.251	主波長	466 nm
7	(0.2774, 0.259	主波長	468 nm
8	(0.2799, 0.271	主波長	471 nm

Blue region

V=250mm/s

7	(0.2605, 0.233	主波長	463 nm
8	(0.2633, 0.242	主波長	468 nm
9	(0.2615, 0.243	主波長	471 nm

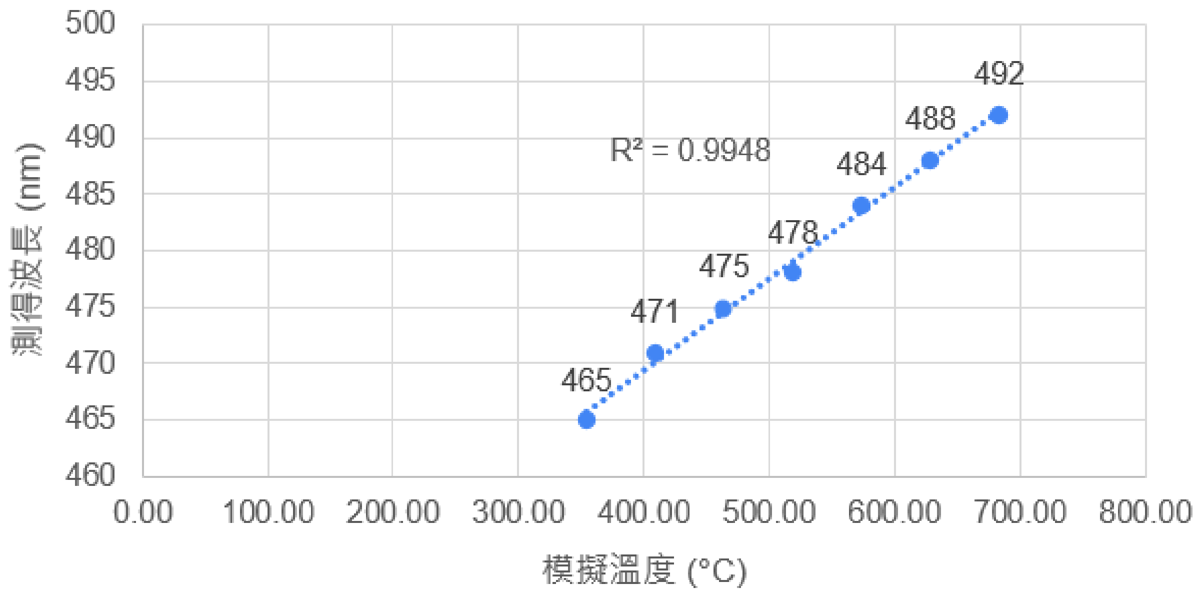
Blue region

Spectral analysis

Surface peak temperature vs primary wavelength

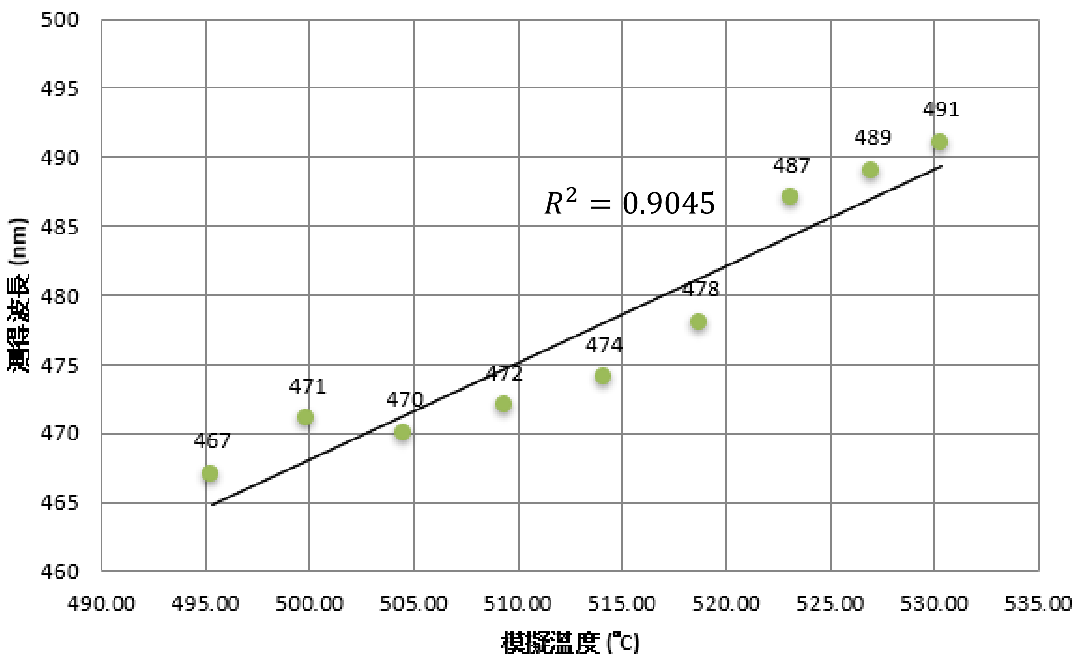
Fixed speed **150mm/s**

Scanning speed 150mm/s: wavelength vs simulated temp.



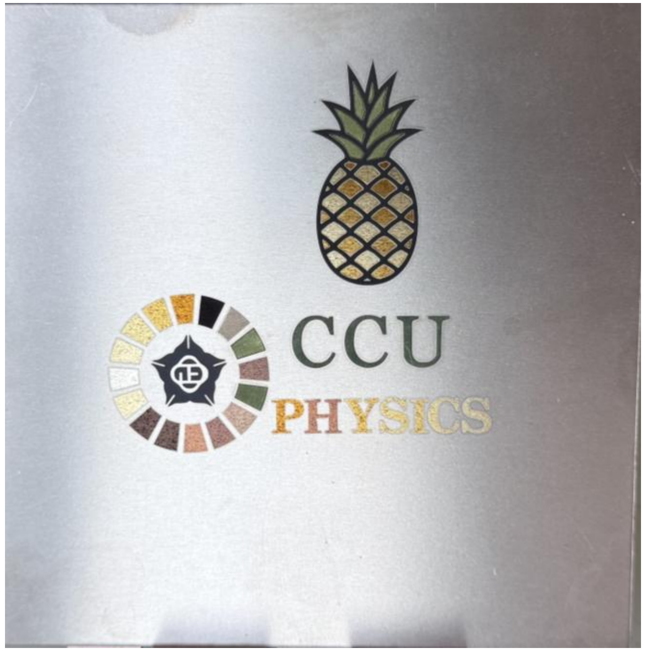
Fixed power **9W**

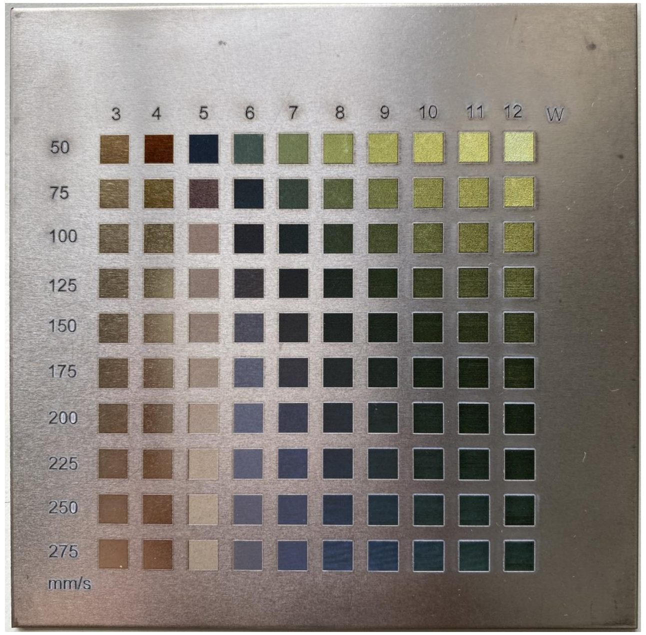
Power 9W: wavelength vs simulated temp.



Conclusion & Outlook

- A wide color gamut can be achieved on titanium surfaces through laser engraving.
- The effects of peak power and scanning speed on surface coloration have been quantitatively characterized.
- The observed coloration originates from thin-film interference caused by laser-induced oxide layers.
- Customized color patterns can be generated through controlled engraving conditions.





Reference

•[1] H. Liu, W. Lin, M. Hong, Surface coloring by laser irradiation of solid substrates, APL Photonics 4 (5) (2019) 051101.

•[2] A.J. Antończak, B. Stępak, P.E. Kozioł, K.M. Abramski, The influence of process parameters on the laser-induced coloring of titanium, Appl. Phys. A 115 (3) (2014) 1003–1013.

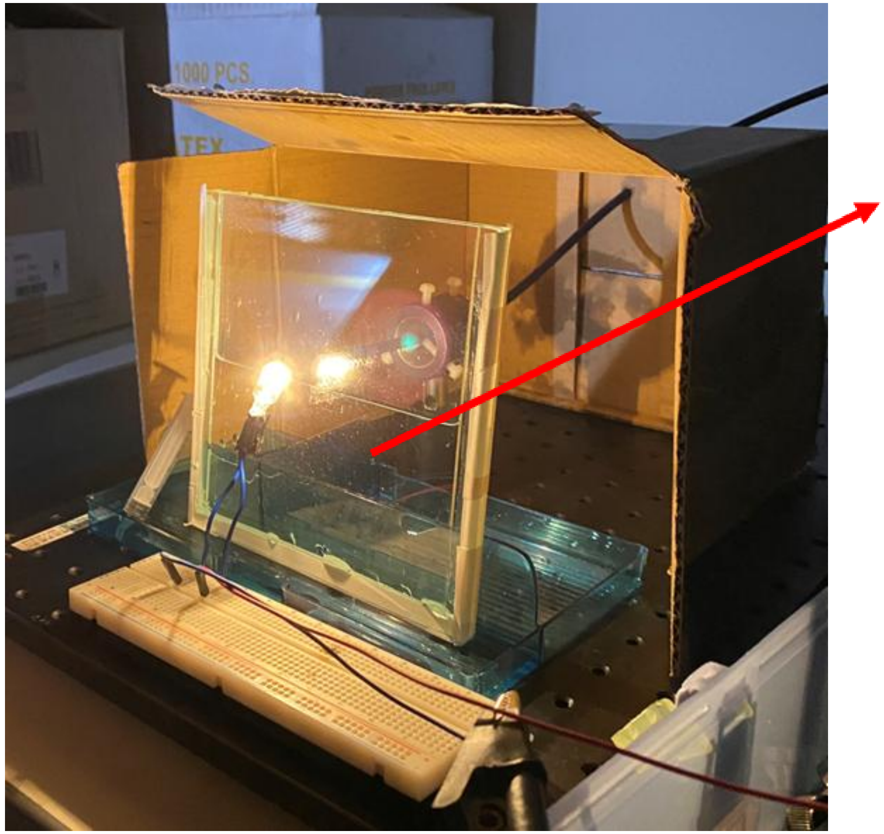
•[3] V. Veiko, G. Odintsova, E. Ageev, Y. Karlagina, A. Loginov, A. Skuratova, E. Gorbunova, Controlled oxide films formation by nanosecond laser pulses for color marking, Opt. Express 22 (20) (2014) 24342–24347.

•[4]光學薄膜於色彩顯示之應用
https://www.ncir.niar.org.tw/Files/Doc/Publication/InstTdy/177/01770480.pdf

Appendix

Light source selection

Methods I (initial design)



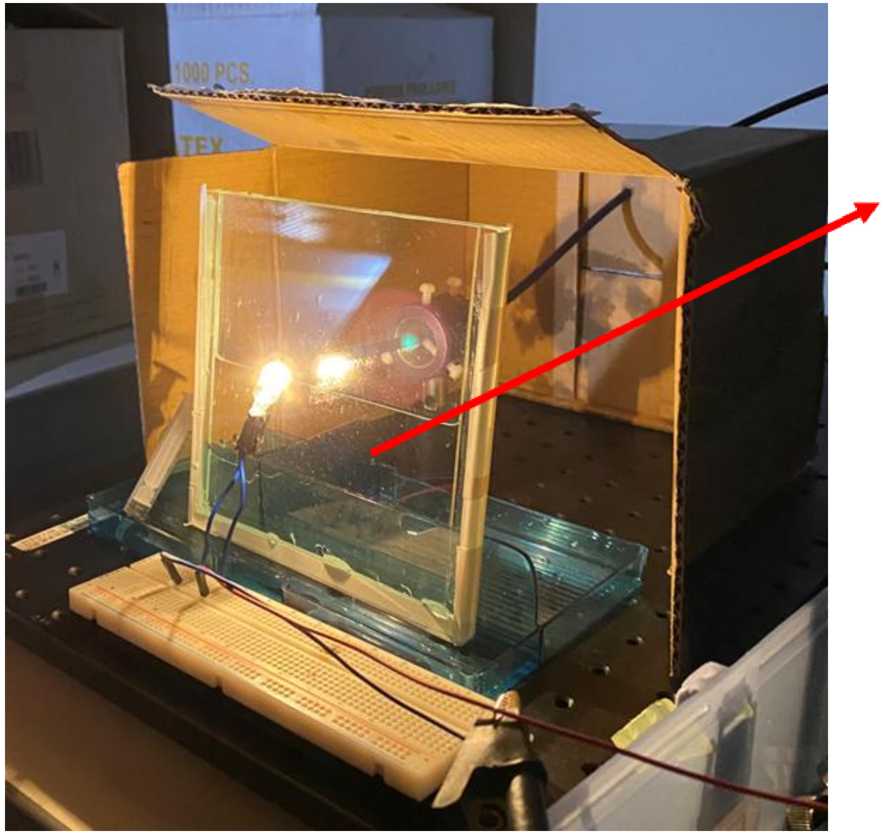
Light passing through water:

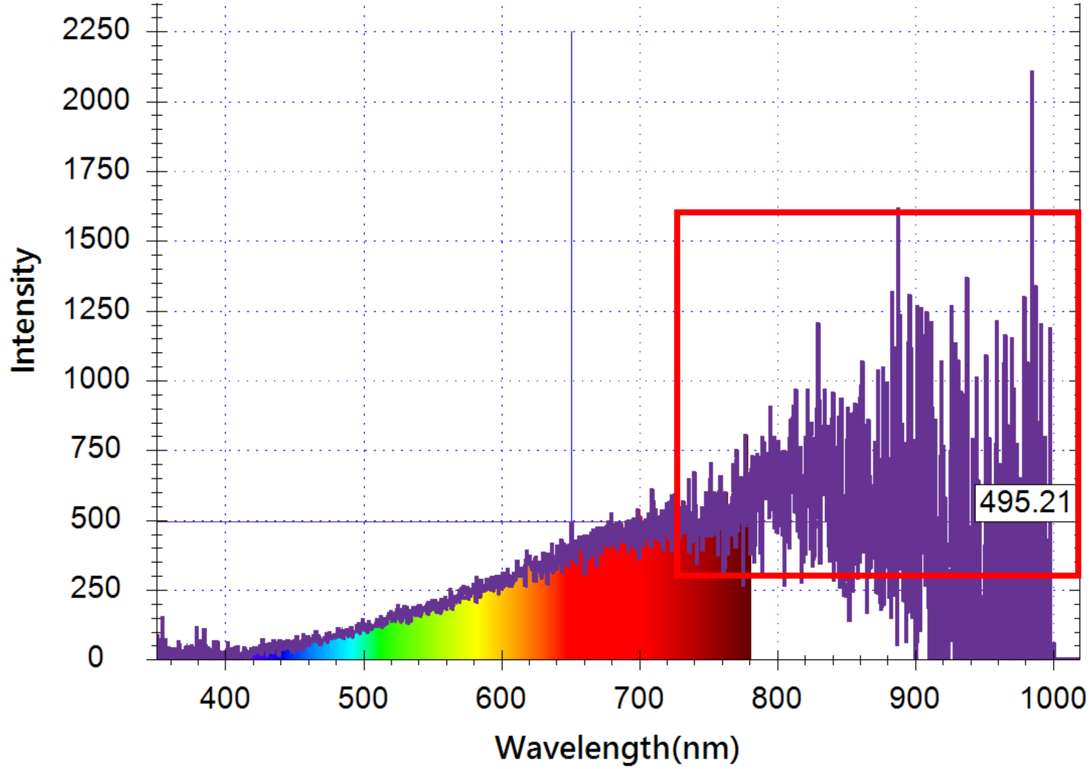
Since incandescent tungsten lamp(鎢絲燈) emits large infrared radiation, placing a layer of water in the optical path can filter out part of the infrared light making the overall light source more uniform and reducing interference from infrared radiation.

However, we still gained so much noisy !

Light source selection

Methods I (initial design)





Spectrum of tungsten lamp after filtering out part of the infrared light.

The noisy still remains, leading inaccurate analysis. Too bad.

Theory

The beam energy of a continuous wave (CW) laser is not uniformly distributed in space; rather, it exhibits a Gaussian distribution characterized by peak energy at the center that gradually decreases toward the periphery. When the laser scans along the x-axis at a constant speed, the surface heat Q inputted into the metal surface is expressed as:

$$Q_{2D}(x,y,t) = \frac{2AP}{\pi\omega^2}\exp(-2\frac{(x-vt)^2+y^2}{\omega^2})$$

- P:Laser output power (W)
- ω:Laser beam radius (m)
- A:Laser absorptivity of the material surface
- v:Laser scanning speed (m/s)
- t:Irradiation time (s)

Theory

The physical model of laser heating in this study is based on the transient heat conduction equation:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q$$

- $\rho C_p \frac{\partial T}{\partial t}$:

Represents the rate of temperature change over time. It depends on the material's density ρ and specific heat capacity C_p, which govern the rate of heat accumulation.

- $\nabla \cdot (k \nabla T)$:

Describes how heat energy diffuses through the three-dimensional space within the material, where k represents the thermal conductivity.

Theory

- The physical model of laser heating in this study is based on the transient heat conduction equation: :

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q$$

- Q:Represents the external heat input. To accurately simulate the continuous wave (CW) laser, the heat source Q is modeled as a moving Gaussian beam distribution.

$$\frac{dX}{dt} = \frac{A}{X}\exp(-\frac{E_a}{RT(t)})$$

- X：Transient thickness of the oxide layer (m)
- t：Time of laser irradiation and heat accumulation (s)
- A：Pre-exponential factor (or reaction constant), related to the material's inherent oxidation characteristic($\frac{m}{s^2}$)
- E_a ：Activation energy of the oxidation reaction (J/mol or kJ/mol)
- R：Ideal gas constant (8.314J/mol·k)
- T(t)：Transient absolute temperature of the metal surface (K)

Theory

- Using heat conduction equation, we can further predict the growth behavior of the oxide layer. Under high-temperature conditions, the growth of the oxide layer on a metal surface typically follows the parabolic rate law.

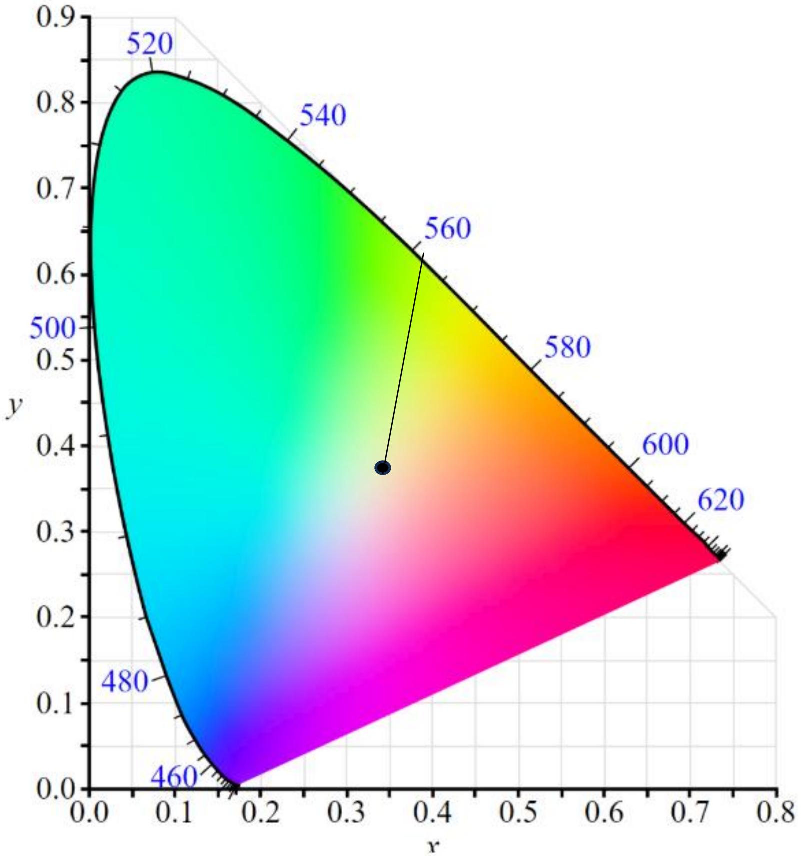
It's growth rate can be described by a differential equation incorporating the Arrhenius equation.

$$\frac{dX}{dt} = \frac{A}{X} \exp\left(-\frac{E_a}{RT(t)}\right)$$

The CIE 1931

We use CIE1931 to analysis

Convert the physical spectral energy distribution into the stimulus values (刺激值) of the three types of photoreceptor cells in the human retina.



CIE XYZ chromaticity coordinates (色度座標)

The spectrum of an object measured by a spectrometer can be used to calculate the tristimulus values according to the corresponding formulas, thereby representing the color of the object.

By converting the spectrum of the sample, the corresponding x-y values can be plotted in the CIE chromaticity diagram to determine the corresponding wavelength.

The CIE 1931

How to calculate?

Step1:

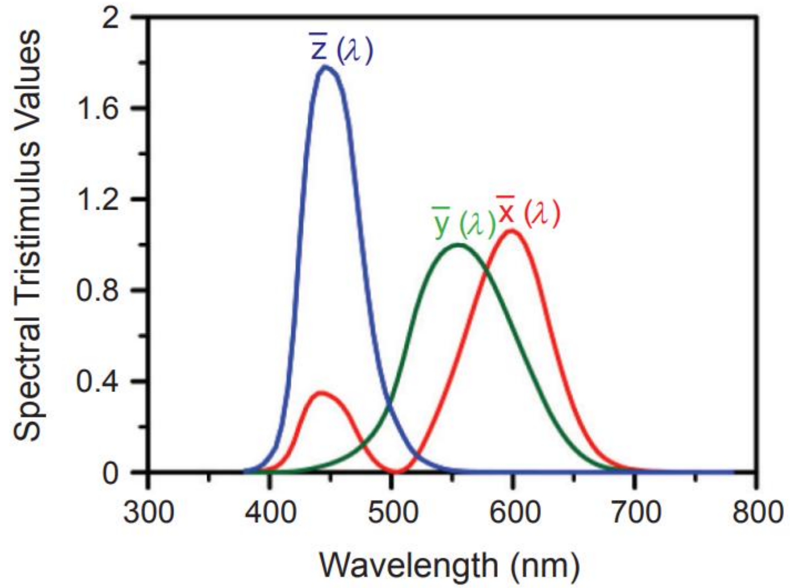
Measured spectrum(待測光譜) $S(\lambda) = R(\lambda) \times I(\lambda)$

In which,

$R(\lambda)$ = Object reflectance spectrum，$I(\lambda)$ = Standard illuminant spectrum (D65，white light)

Step2: Apply the CIE 1931 color matching functions (配色函數)

The three sensitivity curves are the CIE 1931 color matching functions (standard observer with a 2°of view).



$\bar{x}(\lambda)$ = tristimulus values of red

$\bar{y}(\lambda)$ = tristimulus values of green

$\bar{z}(\lambda)$ = tristimulus values of blue

Covered wavelength from 380 nm to780 nm, with an interval of 5 nm.

The CIE 1931

How to calculate?

Step3: Calculate the XYZ tristimulus values

$$X = k \int_{380}^{780} S(\lambda)\, \bar{x}(\lambda)\ d\lambda$$

$$Y = k \int_{380}^{780} S(\lambda)\, \bar{y}(\lambda)\ d\lambda$$

$$Z = k \int_{380}^{780} S(\lambda)\, \bar{z}(\lambda)\ d\lambda$$

$\bar{x}(\lambda)$ = tristimulus values of red

$\bar{y}(\lambda)$ = tristimulus values of green

$\bar{z}(\lambda)$ = tristimulus values of blue

$$k = \frac{100}{\int S(\lambda)\, \bar{y}(\lambda)\, d\lambda}$$

完美反射的白紙(R=100%)的 Y 值等於 100。

normalization constant

The CIE 1931

How to calculate?

Step4: Convert to chromaticity coordinates (色度座標)

By projecting the XYZ three-dimensional space onto a two-dimensional space and normalizing the tristimulus values, the x-y chromaticity coordinates can be obtained.

$$x = \frac{X}{X+Y+Z} \;;$$

$$y = \frac{Y}{X+Y+Z} \;;$$

$$z = 1 - x - y$$

The (x, y) coordinates can represent the chroma and hue (彩度與色相) of any color on the chromaticity diagram; D65 x-y values is $(x_w = 0.3127, y_w = 0.3290)$

干涉$2nd = m\lambda$
d變化很小設m相同
則$\mathrm{d} \propto \lambda$

$$\frac{\partial X}{\partial t} = \frac{\mathrm{A}exp(-\frac{E_a}{RT})}{2X}$$

$$X(t,T) = \sqrt{d_0^2 + \int_0^t \mathrm{A}exp(-\frac{E_a}{RT(\tau)})d\tau}$$

$$X(t) \approx \left[X(T_{max})\frac{E_a}{2RTmax}\right]T + \left[X(T_{max}) - X(T_{max})\frac{E_a}{2RTmax}\right]$$

$X^2 \approx \int_0^t \mathrm{A}exp(-\frac{E_a}{RT(\tau)})d\tau \approx \mathrm{A}exp(-\frac{E_a}{RTmax})\tau_{eff}$極短時間

$$X(T_{max}) \approx \sqrt{A\tau_{eff}exp(-\frac{E_a}{2RTmax})}$$

$$X(t) \approx X(T_0) + X'(T_0)(T - T_0)$$

$$\Rightarrow \lambda \propto \mathrm{d(T)} = \mathrm{m} \cdot T + \mathrm{C}$$