Material Design and Fabrication of Structural Color using a Biomimetic Approach: Mystery of *Morpho*-Butterfly's Blue

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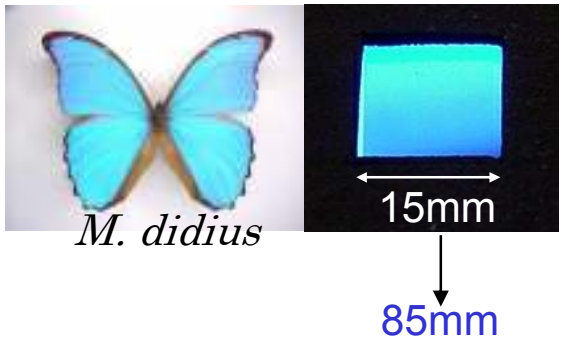
2. SPring-8 (RIKEN Harima Institute)



OUTLINE

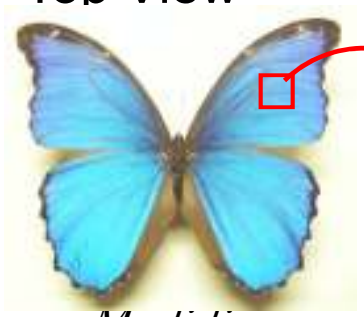
1) Mystery of *Morpho*-blue : Principles
2) Attempt at Reproduction : Process
Results & Examinations
3) Development : Mass-production,
in Application studies Large Area Fabrication,
Theoretical study on
the Role of Randomness.

JAFOE symposium @ Rihga Royal & NCB Osaka, 2011 June 5- 8

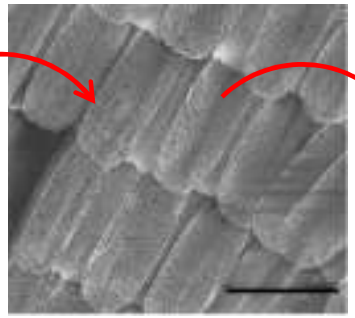
Principles of *Morpho*-type coloration

Blue but Pigment-Free & High Reflectivity. → *Interference Effect* of Periodic Structure.

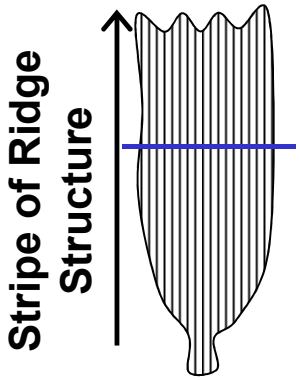
Top View



M. didius

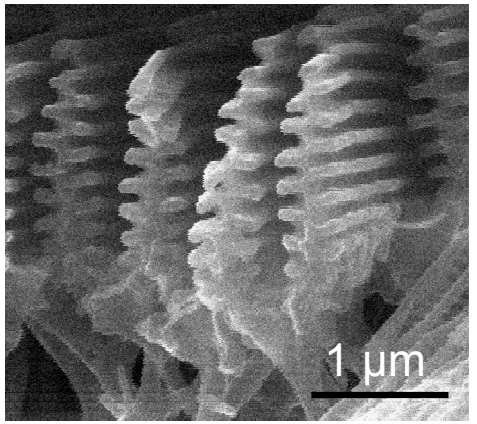


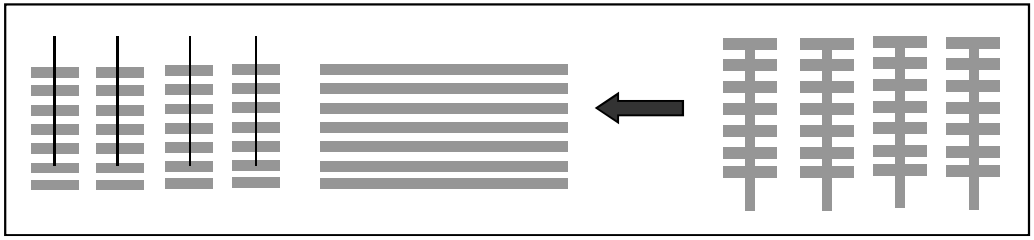
100μm



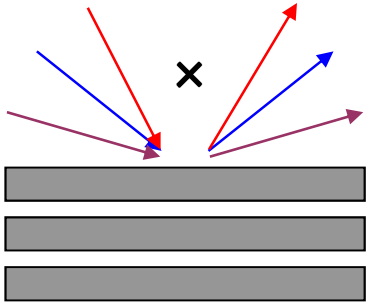
Cross sectional Side View

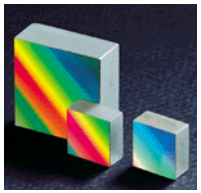
n=1.0
vs
n=1.6





grating model or layered model





High Reflelectivity
Interference

Contradiction

Angular dependence of λ is extremely Low (not multi-color)

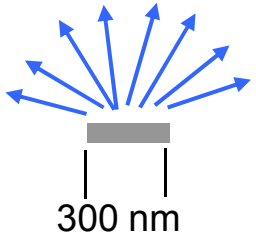
However, a mysterious feature…

“Interference, but Single color & Wide angle.” Why?

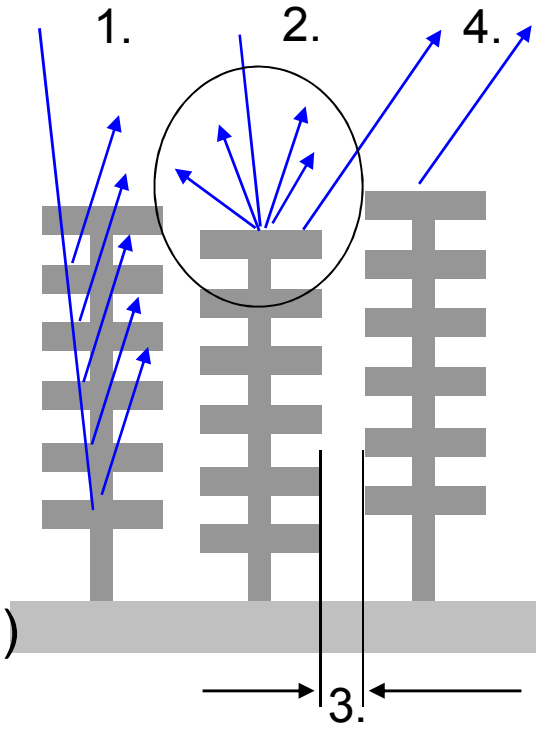
Discrete Multilayer

1. **Blue** is produced by interference within a single discrete multilayer (regular structure)

2. Blue is diffracted from the small width (in a **wide angle**)



Side View



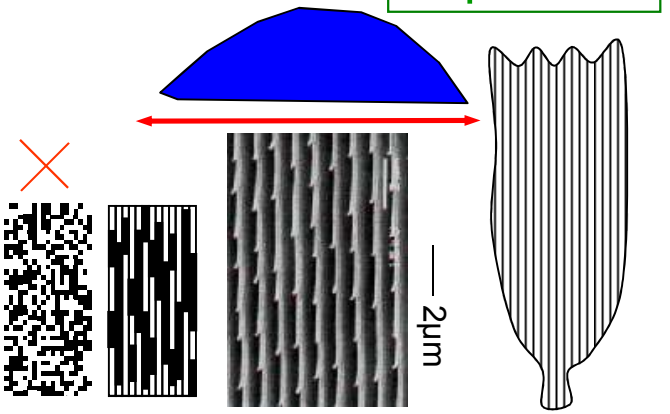
3. Small gap makes **high reflectivity**

5 principles

4. Randomness (height & In-plane) **prevents the multi-color** interference (irregular structure)

5. Quasi 1 -dimensional structure

Top View

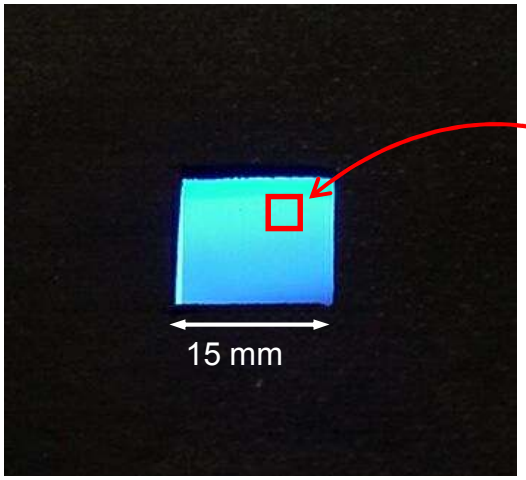


S. Kinoshita et al.
Proc. R. Soc. Lond. B269, 1417 (2002).

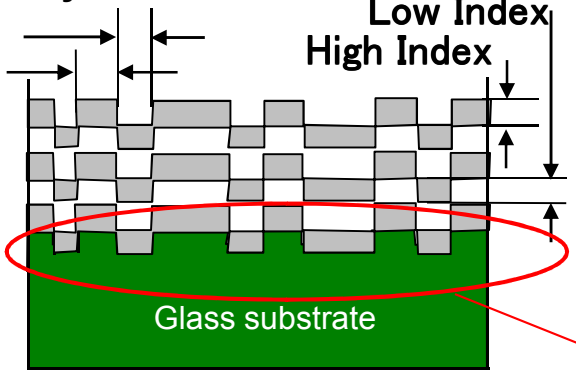
How to Prove it ?

Pigment free

Simple Fabrication Process by Extracting the Minimum Essence of Principles

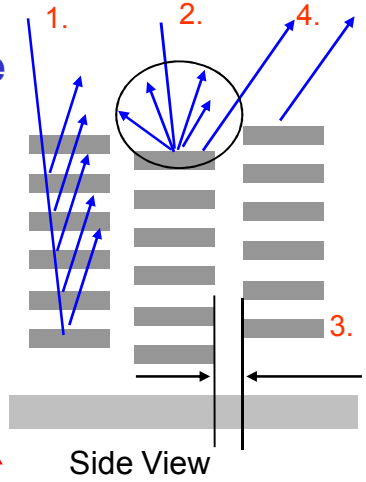


Width & Gap【~300 nm distributed randomly】



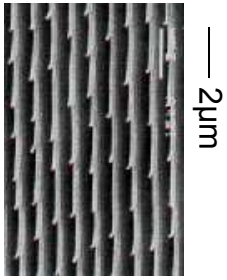
Reproduction of *Morpho*-blue (high reflectivity,Blue in wide angular range, 1-dimensional anisotropy)

A. Saito, S. Kinoshita et al., Proc. SPIE, 5526, 188 (2004).

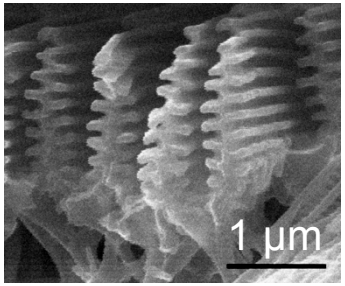


Side View

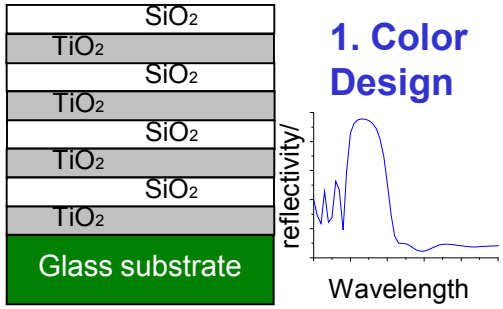
Top View



Morpho Didius

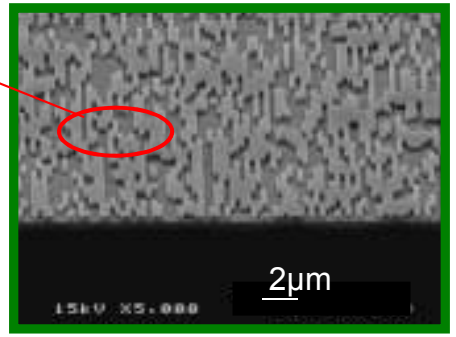


Process



1. Color Design

+

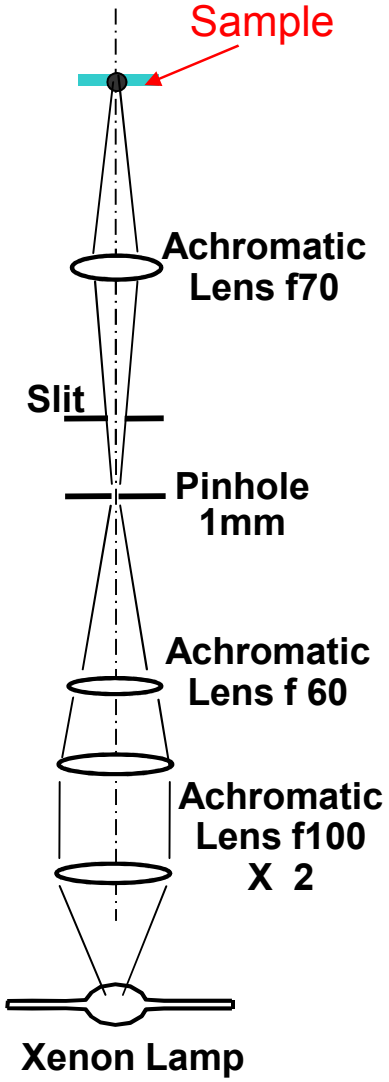


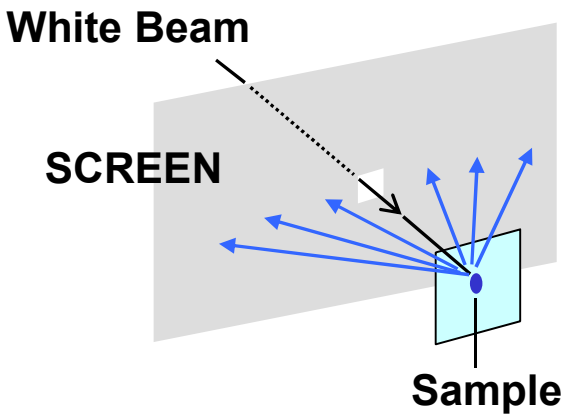
2. 3. 4. 5. Semiconductor Technology

1. interference in a multilayer.
2. diffracted from small width.
3. Small gap ➔ high reflectivity
4. Randomness prevent the multi-color.
5. Quasi 1-dimensional pattern.

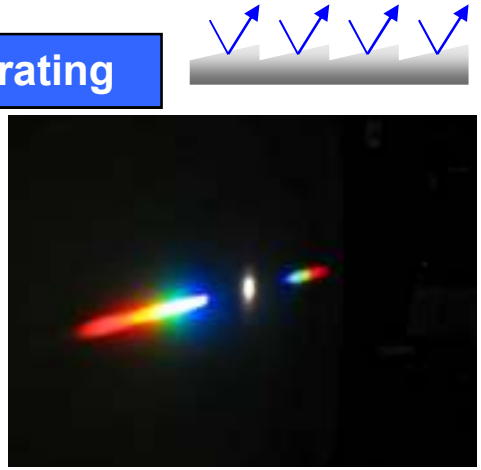
Optical Measurement 1. ~ Reflective Patterns ~

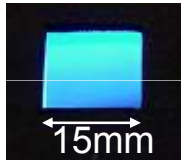
Set up



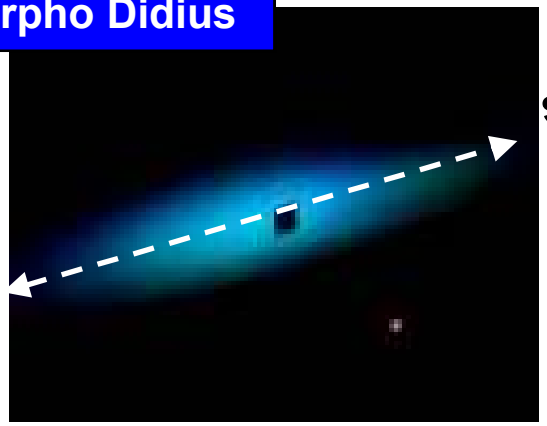


Grating



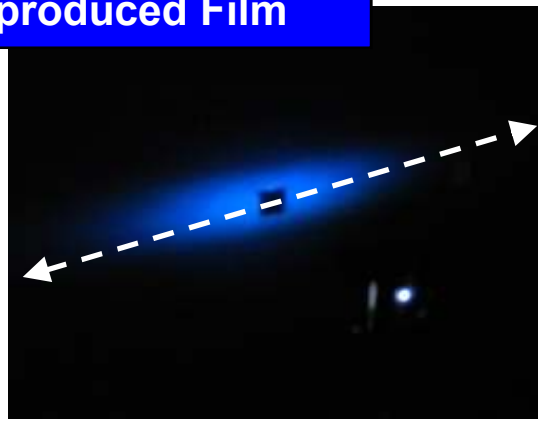


Morpho Didius



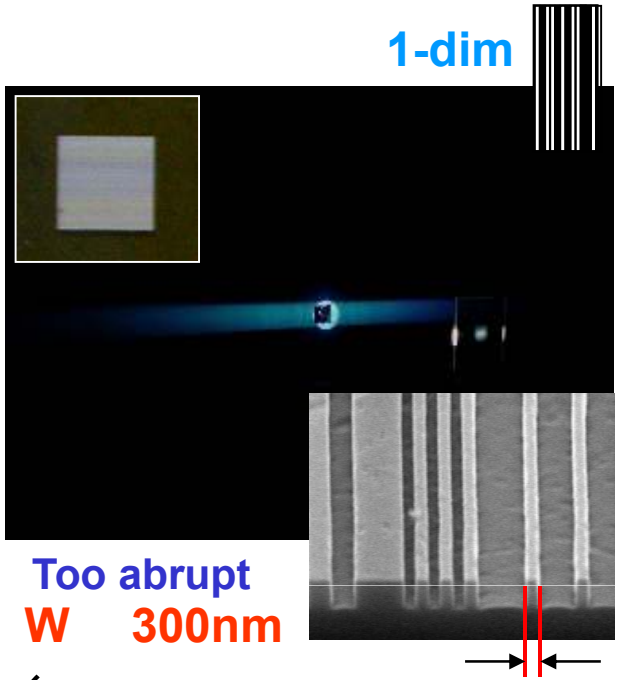
Scan Direction

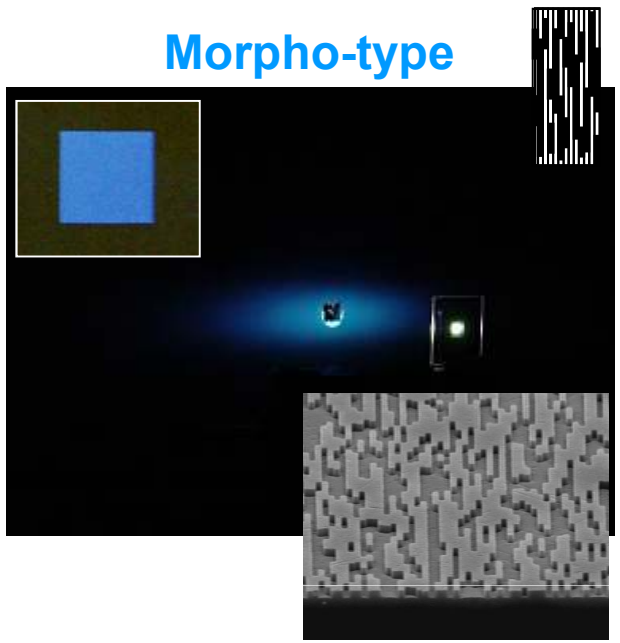
Reproduced Film



Sharp single blue coloration & Anisotropic distribution

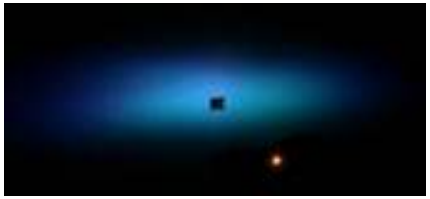
Examination: The Role of the Nano-scale Randomness





(*Width Dependence*, 1-dim)

W 900nm



Real Morpho:
Morpho didius

The optical property depends on the parameters (100nm order) of the substrate (patterns, width, depth).

Possible Industrial Applications

Decoration Films

Articles
(Portable phone,
Watch, etc.)

Cosmetics (Powder)

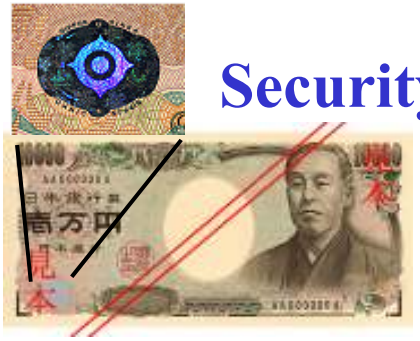
Eye shadow, manicure,
Hair colorings, etc.

color quality is different from conventional one

Displays
Posters

requirement

- **High Efficiency**
- **Anti-Interference**
- **Single color in Wide Angle**



Security

Paints, Ink

Textiles

Sign Board, Logo

Advantages of the Structural Color

1) **Long lifetime (fadeless).**
2) **Thin & Light.**
3) **Low Power : Use of Light from Outside.**
   (Back Light can be saved)
4) **Pigment Free (Ecological)**
   ➔Saving Materials.

For Industrial Applications,

1. Mass-Production, 2. RGB, 3. Control, 4. Randomness, 5., ….

What is necessary for Applications ?

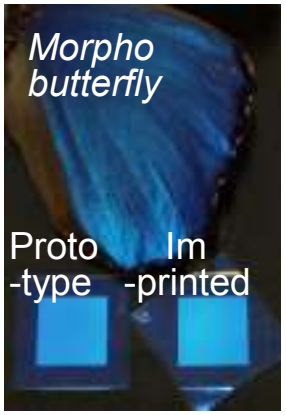
Electro
-forming

1. Mass-production

Nano-imprint

2. Large area

fs Laser



Throughput x 1000

UV

Rasin

Glass

Quartz

duplicate

Glass

Quartz

A.Saito et al., Proc. SPIE 6327 (2006) 1- 9.
A.Saito et al., JVST. B24 (2006) 3248-3251.

Done w/ success

Patented 2008.9.27
(applied in 2003)

3. Substrate-Free

Film

A Inc. B Inc. C Inc.

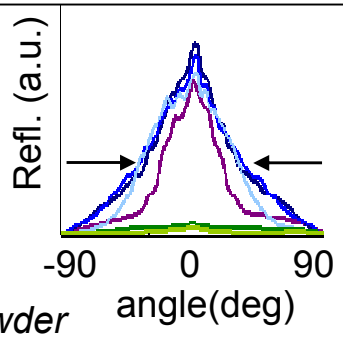
Logo, Display, etc.

Powder

Cosmetic

Done w/ success

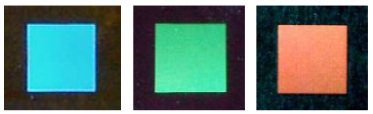
4.Control:Angular distribution



A.Saito et al., Proc.SPIE 6767 (2007) 1-8.
A.Saito et al., J. of Soc. Powder Technol. Jpn 45 (2008) 180-186.

Done w/ success

5. RGB

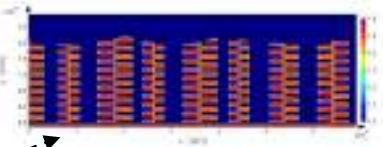


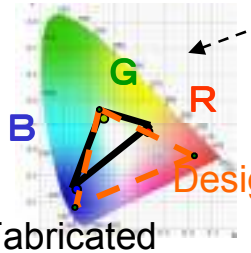
A.Saito et al., J. Surf. Sci. Soc. Jpn. 28 (2007) 414-420.

FDTD

6. Simulation

6. Control :
Color phase





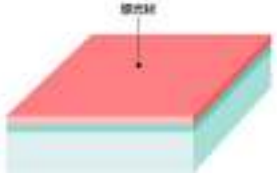
Precise design

A.Saito et al., J. Nanosci. Nanotechnol. (2011)

A.Saito et al., Proc.SPIE 7205 (2009) 1

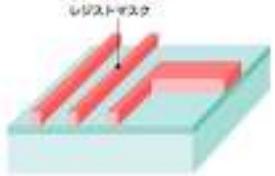
Process

by e-beam Lithography



1) Resist coating /Glass Substrate

2) e-beam Patterning

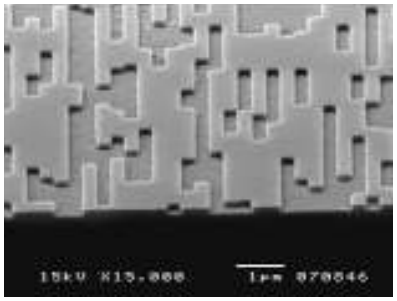


3) Development

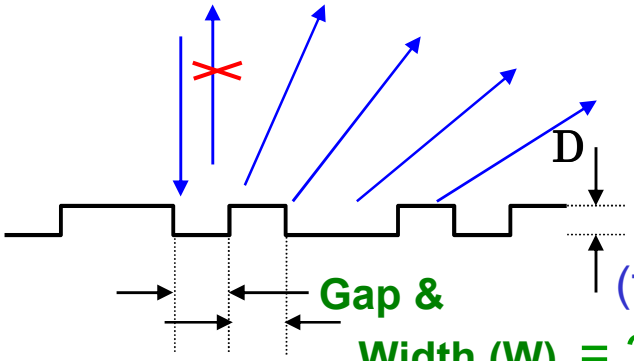
4) Etching (Dry)

1) Nano- Patterning of Substrate

SEM image (before deposition)



Patent : SAITO et al, (2001-241496), (2003-391572)

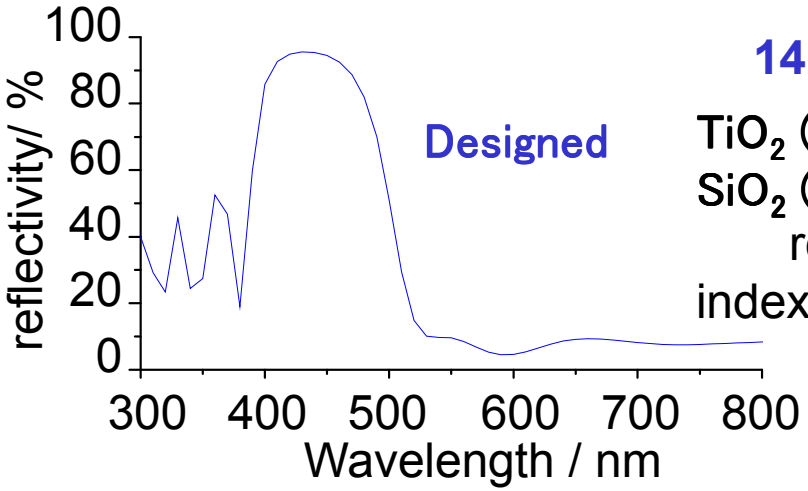


110nm
(to prevent normal reflection)

Width (W) = 300 x (2000±σ) nm

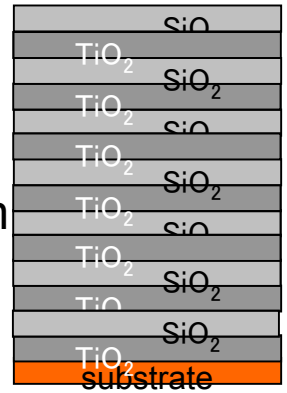
Narrow width & gap, Quasi 1-dim ➔ Controlled Randomness

2) Multilayer Deposition (by e-beam Deposition)

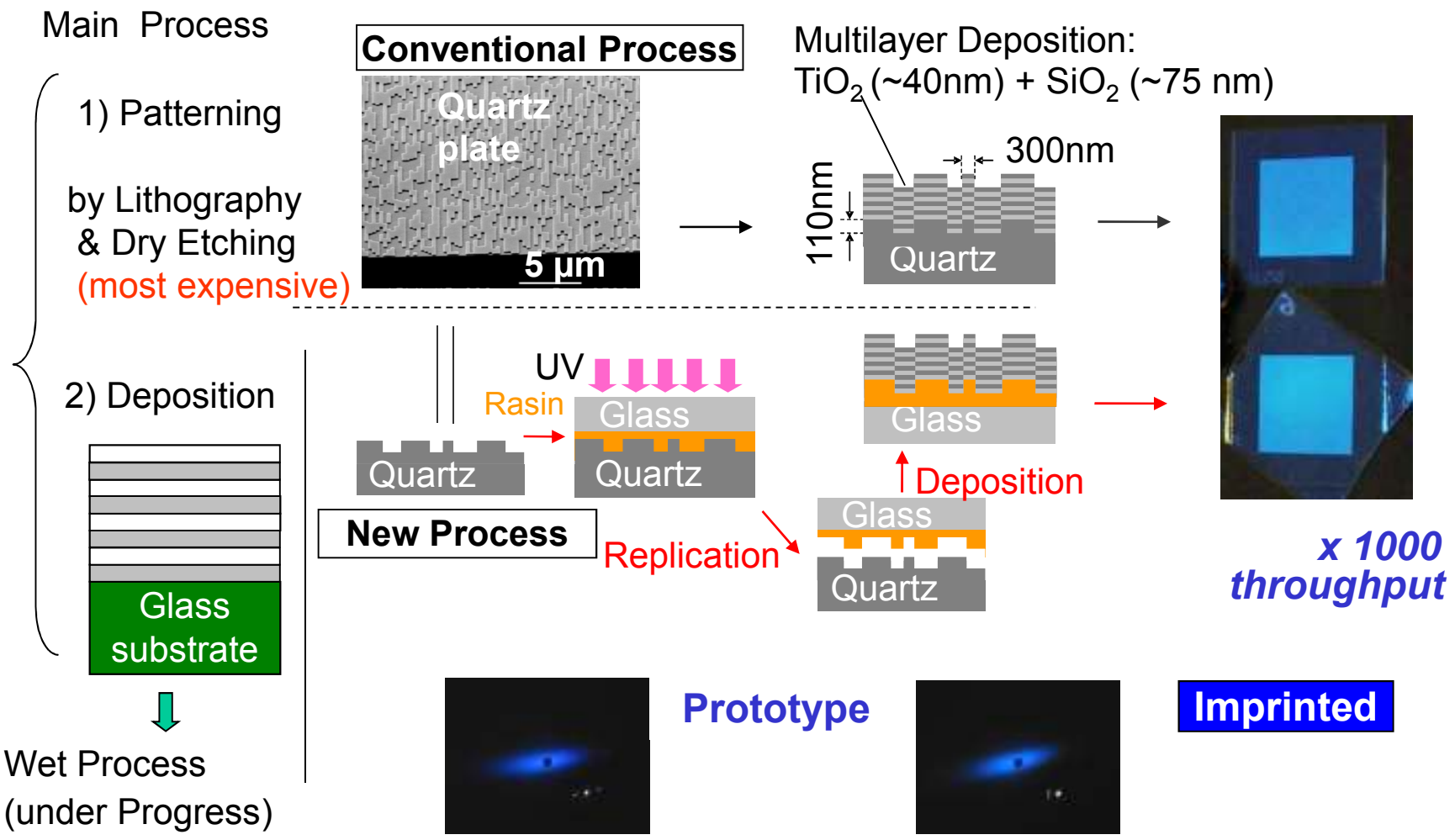


14 layers, totally 936 nm

TiO_2 (40 nm) 2.5
SiO_2 (75 nm) 1.5
refractive ↑
index @ 500 nm



1. Mass-Production by Nano-Imprint (~2007)



Principal properties

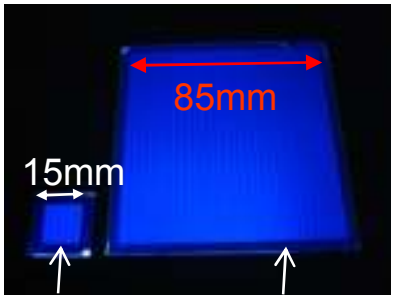
➔ reproduced by the imprinted film, too

2. Large Area Fabrication

Why necessary ?

A. Mass-Production

Large Mold

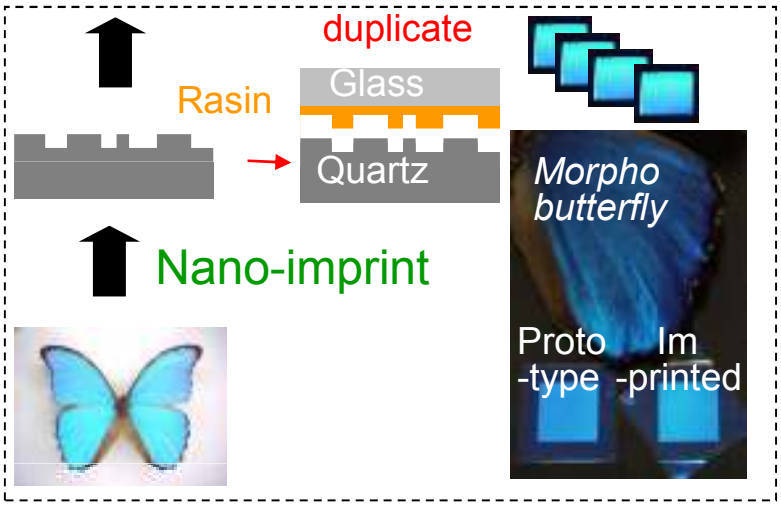


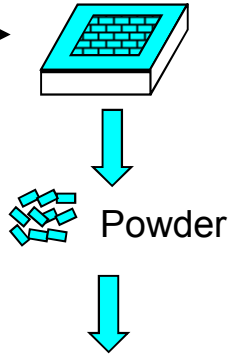
／20 hours ／7 min.
~ x 5000

Electro-forming

femto-s Laser

Mass-production





B. Requirements for

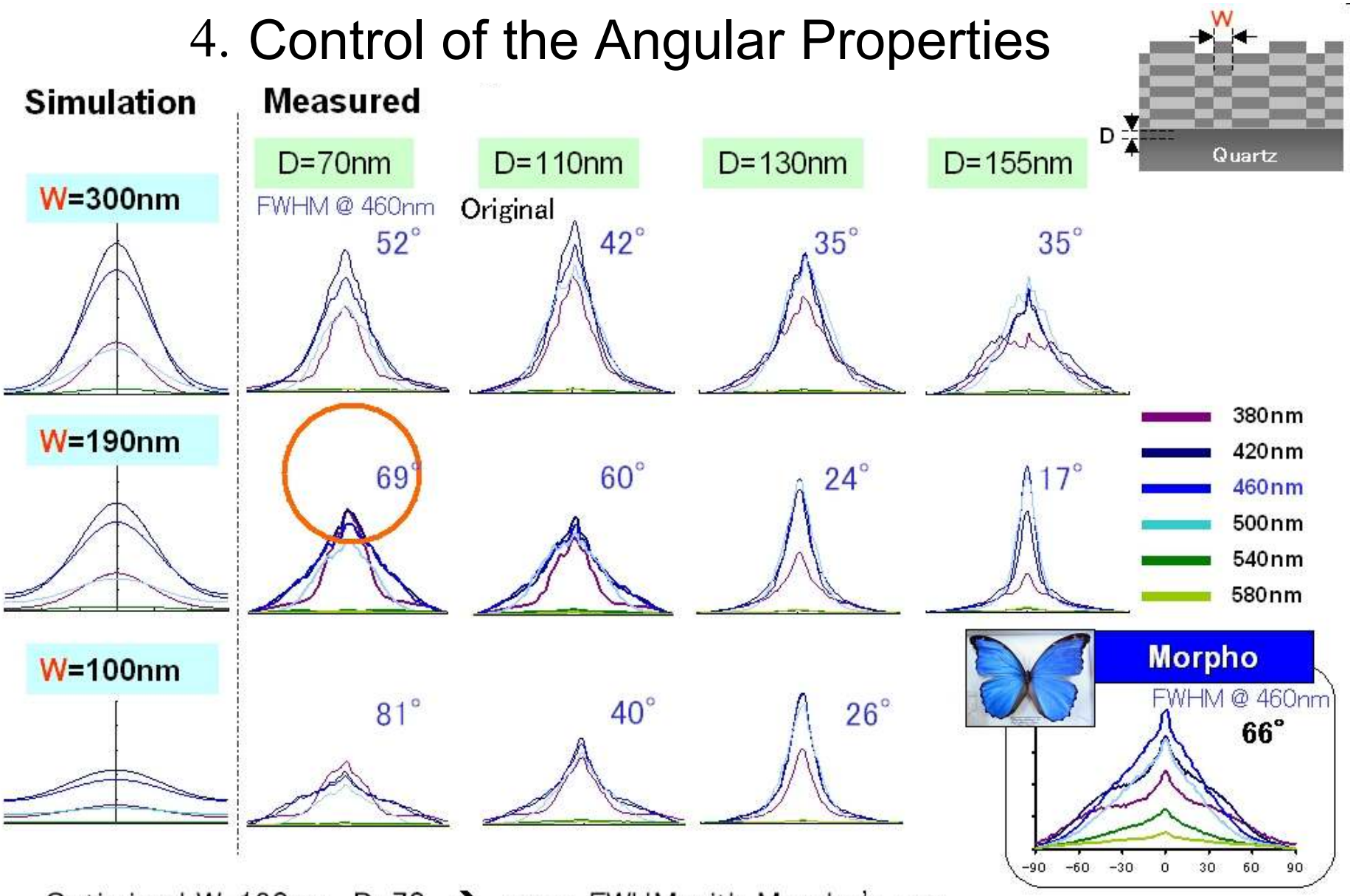
JST Project（2008～2009）
Seeds Innovation

Building materials

Long Lifetime, Brilliant, Ecological in Outside.

Logo Plate, Signboard, etc.

4. Control of the Angular Properties



Optimized W=190nm、D=70 ➔ same FWHM with Morpho's one

Best conbination of W & D ➔ FWHM was optimized

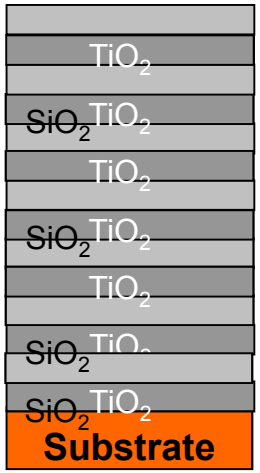
5. RGB

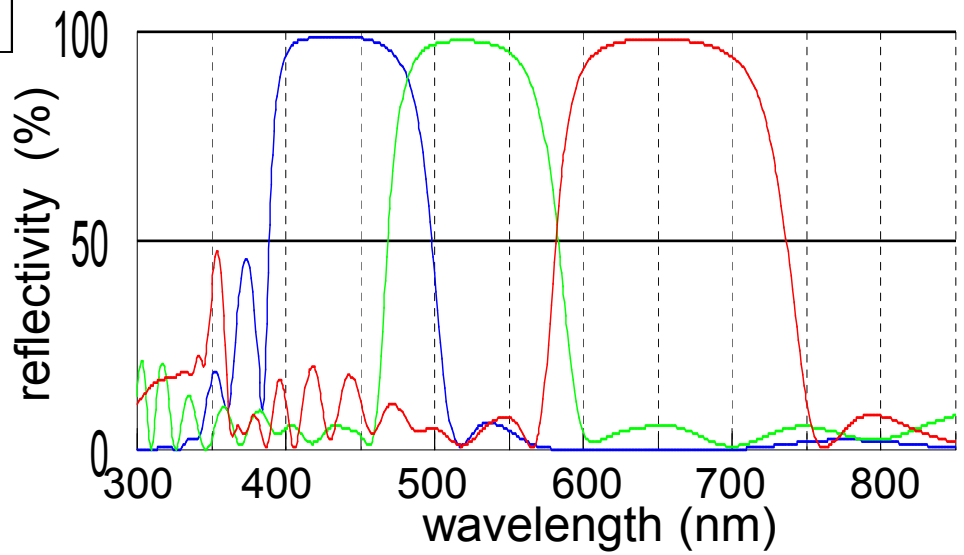
N-index @ 500 nm

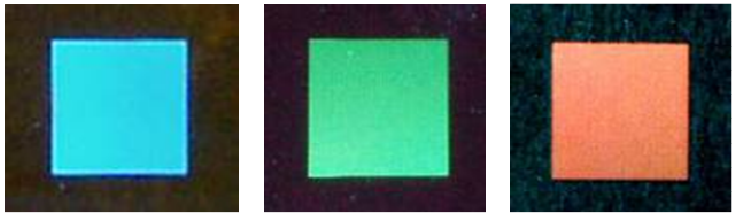
TiO_2 2.5
Ta_2O_5 2.2
SiO_2 1.5

e-beam Deposition

14 layers, 936 nm totally
TiO_2 (~40 nm) , SiO_2 (~75 nm)
16 layers, 1820 nm totally
TiO_2 (~80 nm) , SiO_2 (~110 nm)
16 layers, 1600 nm totally
Ta_2O_5 (~66 nm) , SiO_2 (~90 nm)







Single Color &
High Reflectivity
in Wide Angular Range
for RGB

How to calculate the optical role of randomness?

Basic concept : FDTD (finite-difference time domain) method

$$\nabla \times \vec{E} = -\mu \frac{\partial \vec{H}}{\partial t}$$

Maxwell's equation

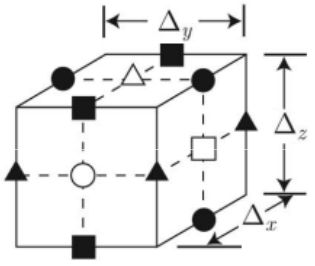
transformed into the difference equation

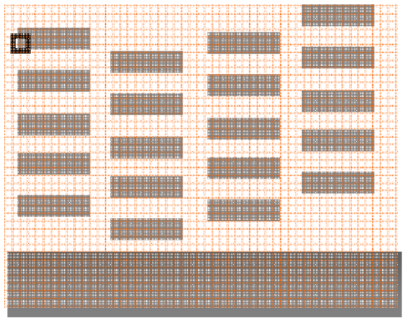
$$H_z\big|_{i,j,k}^{n+1/2} = H_z\big|_{i,j,k}^{n-1/2} + \frac{\Delta_t}{\mu \Delta_y}\left(E_x\big|_{i,j+1/2,k}^{n} - E_x\big|_{i,j-1/2,k}^{n}\right)$$

$$-\frac{\Delta_t}{\mu \Delta_x}\left(E_y\big|_{i,j+1/2,k}^{n} - E_y\big|_{i,j-1/2,k}^{n}\right)$$

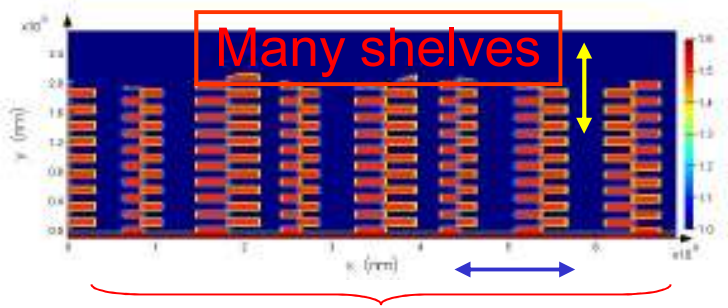
※ $$H_z\big|_{i,j,k}^{n+1/2} = H_z\left(i\Delta_x, j\Delta_y, k\Delta_z, (n+1/2)\Delta_t\right)$$

Divide the space into a large number of small blocks (Yee Cell)





Model of the scale

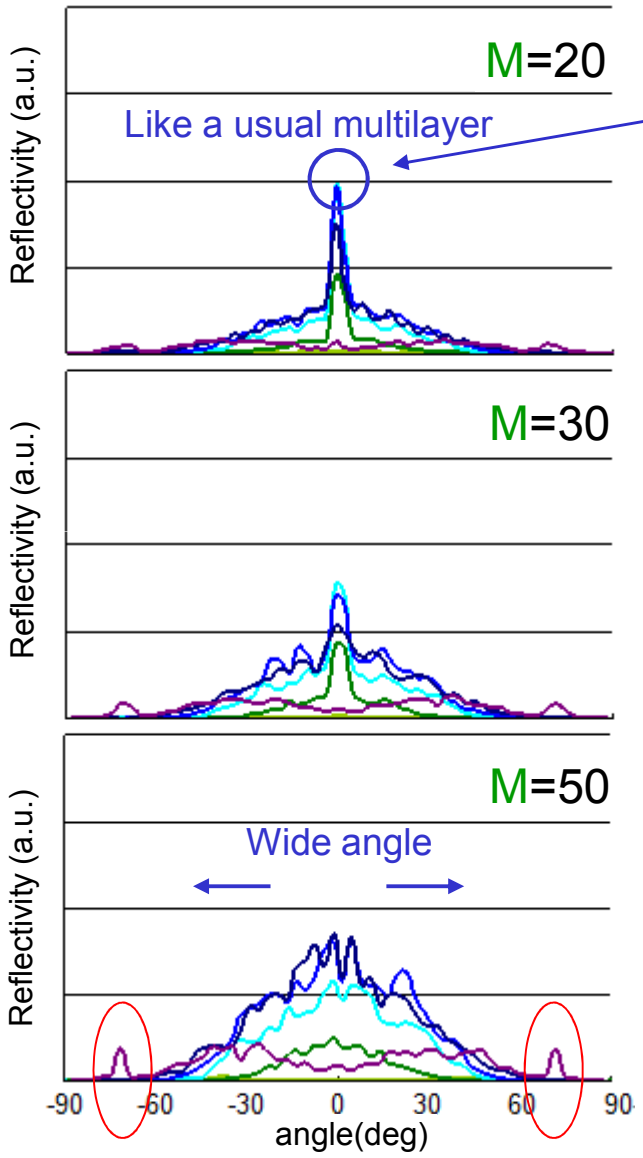


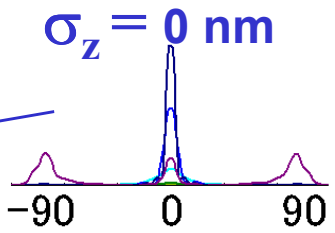
FDTD enables us to treat the random (non-analytical) structures.

optical effects of the randomness

How does the different kinds of randomness affect the optical properties ?

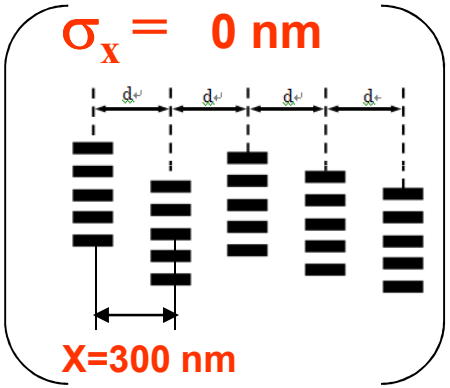
the Optical Role of Randomness in Structure





M: increase

with σ_z = 50 nm

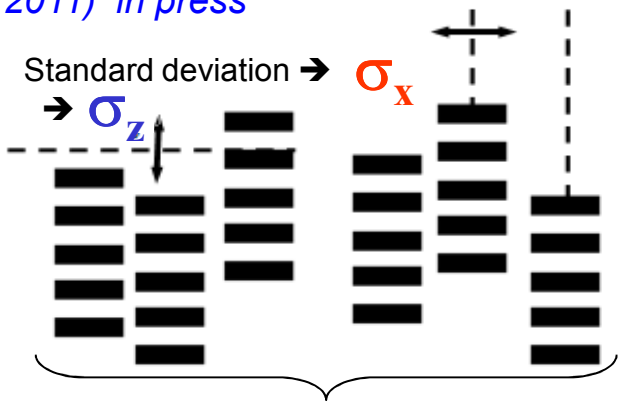


Wide angle, but Grating effect

σ_x is introduced (30 nm)

Grating is reduced, More smooth in short λ

A.Saito et al., J. Nanosci. Nanotechnol. (2011) in press



number of shelves = M

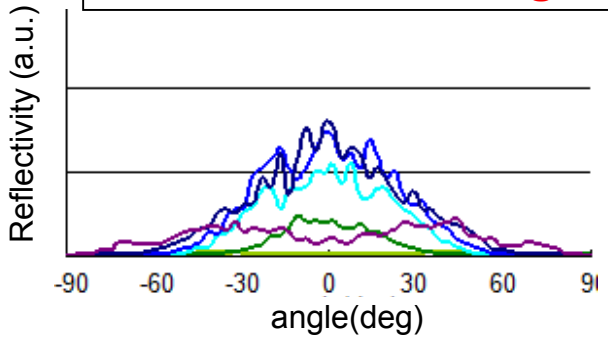
The role of

σ_z ➔ wide angle

σ_x ➔ anti-grating

M > 50 ➔ activate the function

Incohe. ➔ anti-fringe



Global Summary: Interaction of Photon vs. nanoMatter

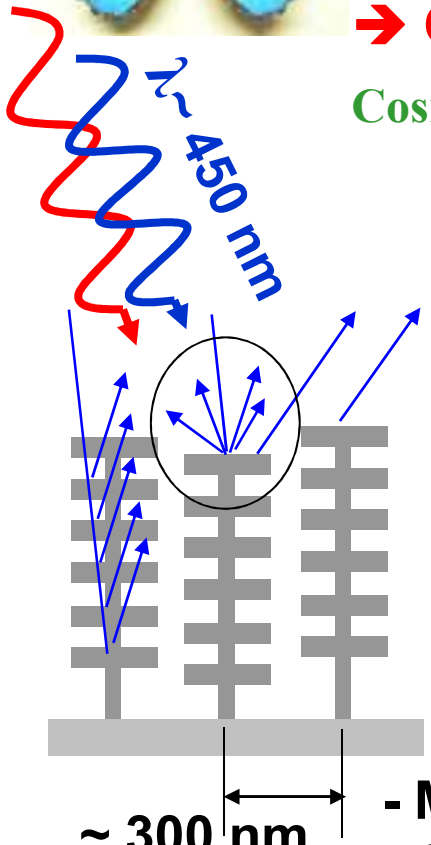
Diffraction
Scattering
Interference
➔ Color sensitive

Cosmetics Decorations

Ink, Paint Textiles

Logo plates, etc.

Displays



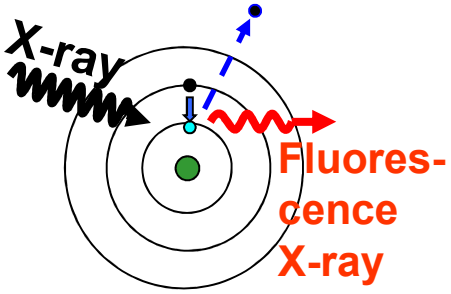
next step

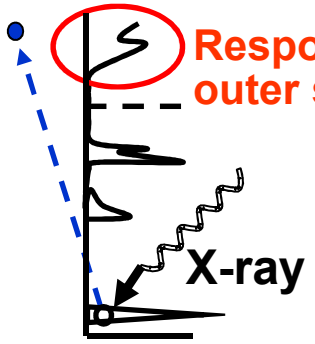
- Mass-production
- Control of Color

etc.

λ➔ 0.01 ~ 10 nm
➔ Core Excitation
➔ Element Sensitive

anoher type

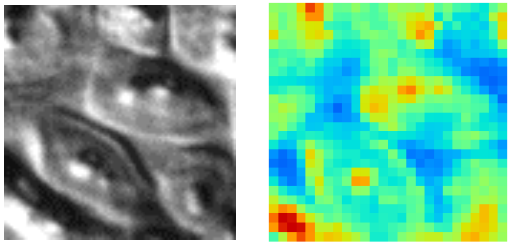




X-ray Fluores. ⇩ **chemical analysis on** ⇩ **STM**

1. biological cells

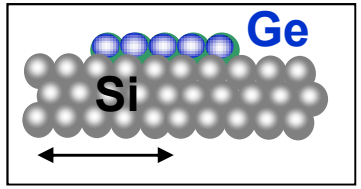
Nomarski Zn Mapping



< sub μm

A.Saito et al: Cancer Res. 65 (2005), 4998.

2. atom, molecule



< 1 nm

A. Saito et al.: Surf. Interface Anal. (2008), 1033

Further References: **Versatile Photon- Matter Interactions in Interdisciplinary Fields**

SAITO Akira 1) Osaka Univ. 2) SPring-8 3) PRESTO, JST

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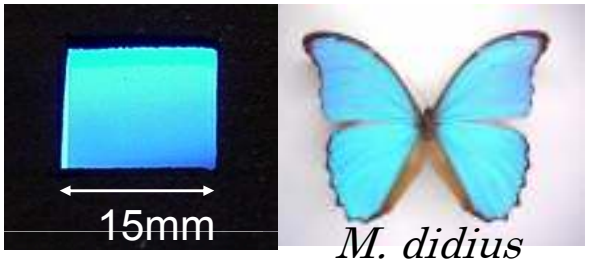
1. Artificial *Morpho* Butterfly's Color

Biological applications

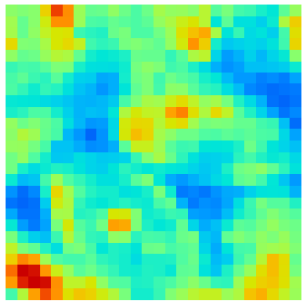


Surface Sci.

Nomarski

20 μm

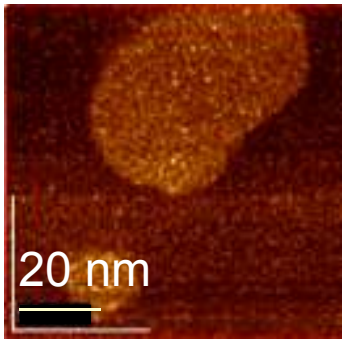
Zn distribution



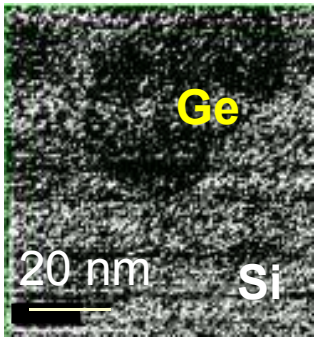
20 μm

SR

STM image



Ge distinction



High Resolution Elemental Analysis

~ from 2. *Single Biological Cell* to 3. *Single nm* Scale ~