Can Thin Film Alloy Refractive Index Be Accurately predicted?

---Theoretical & Experimental Study Thin Film Alloy AgZn Refractive Index

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Abstract

- The optical refractive index and electrical resistivity ρ of Silver Zinc alloy were studied experimentally by a co-sputtering method.
- Currently, the theories on alloys refractive index are too complex, dependent on too many factors, so it can still only be a semi-practical prediction.
- In this study, a new theoretical method was developed to simplify the calculation of silver alloy IR refractive index, and also valid experimental condition was found.
  - (1) Theoretically, the refractive index ratio n_{alloy}/n_{Ag} between silver and its alloy at IR region is derived, a way to cancel out most factors so that it only depends on free electron density n_e and the film resistivity ρ
  - (2) Experimentally, this assumption was approximately met at a special conditions
  - (3) The experimental results agreed well with this simplified calculation.
- Further how the zinc electrons contribute to the optical and electrical properties in low Zn concentration AgZn alloy (<10%) was experimental presented and discussed in this study.

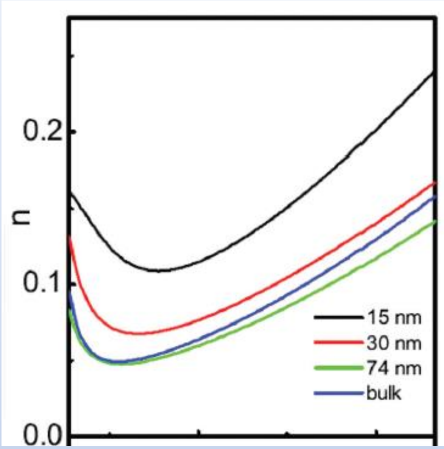
Introduction

- We are initially curious
  - Why are there no accurate theory calculations for metal thin film refractive index?
- Can we derive such an accurate theoretical calculation?
- Can we prove the theory by experiments?

Why refractive index calculation is hard to meet thin film value

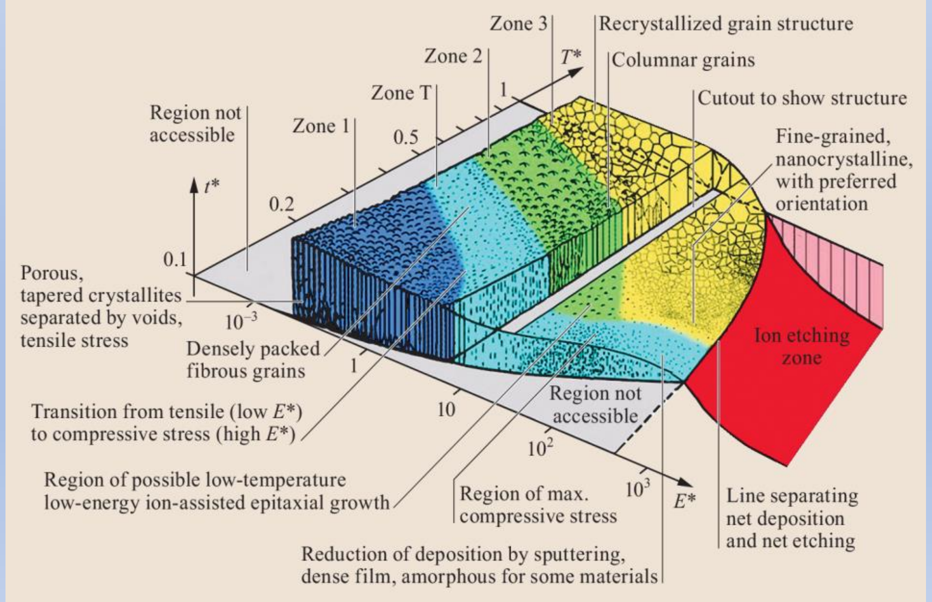
- The thin film refractive index is dependent on too many factors,
  - up to multiple hundred % impacting on the index

- Complexity physics for thin film alloys optical and electrical properties
  - Alloy Atom structure, Crystal or amorphous/Crystal structure
  - Crystal defects/ Materials impurity
  - Film thickness / roughness / Grain size
  - Substrate materials
  - Ambient environmental conditions (temperature, humidity, queue time)
  - Deposition condition: pressure/ temperature / power / gun to substrate distance/…



Ref. 3
silver thin film refractive index varied more than 2 times

Thornton diagram: thin film properties varied significantly as different deposition conditions



Theory on metal properties calculation

Free electron model Assumption: (function of X, E(electric field), ω (frequency), τ(collision time))

Dielectric Constance ε_r definition (function of X, E)

Dielectric Constance ε_r is function of ω, τ, ω_{pe} frequency, collision time, plasma frequency, which is function of electron density ne)

optical and electric properties

More In detail

- Drude-Lorentz Model assumptions: (widely used, especially for group I and XI elements)
- In math: $-eE(t) = m_e \frac{d^2x}{dt^2} + \frac{m_e}{\tau}\frac{dx}{dt}$ (1)
- The Solution is $X = \frac{eE}{m_e(\omega^2 + i\frac{\omega}{\tau})}$ (2)
- The electric displacement field: $D \equiv \varepsilon_0 E + P \equiv \varepsilon_r \varepsilon_0 E$ (3)
  - And polarization $P = -e \cdot n_e x$ (4)
- Substitute Eqs.(2),(4) into Eq. (3) ➔

  dielectric constant $\varepsilon_r = 1 - \frac{\omega_{pe}^2}{\omega^2 + i\frac{\omega}{\tau}} = 1 - \frac{\omega_{pe}^2 \tau^2}{1+\omega^2\tau^2} + i\frac{\omega_{pe}^2 \tau^2}{\omega\tau(1+\omega^2\tau^2)}$ (5)

  Where ω_{pe} is plasma frequency, $\omega_{pe}^2 = \frac{n_e e^2}{\varepsilon_0 m_e}$ (6)
- And Ohm's & Newton's laws ➔ Collison time $\frac{1}{\tau} = \frac{n_e e^2 \rho}{m_e}$ (7)

e: is electron charge
m_e is electron mass
τ: is the collision time
ω: is frequency
ω_{pe}: is plasma frequency
n_e is electron density
E: electric field
D: electric displacement field
P: polarization
ε_0: is dielectric Constance in vacuum
ε_r : is relative dielectric Constance
ε_1: is real part of dielectric Constance
ε_2: is imaginary part of ε_r
ρ: is resistivity

Refractive Index calculation was simplified from literatures

- Refractive index mathematically

$$n + ik = \sqrt{\varepsilon_r} = \sqrt{\varepsilon_1 + i\varepsilon_2}$$

Calculation Eq(5) can be simplified by

- **Assumption 2**: $|\varepsilon_1| \gg |\varepsilon_2|$;
  - Valid for group 1 and 11

- **Assumption 3:** $\omega^2\tau^2 \gg 1$;
  - Valid for wavelength < $3\mu m$

$$\varepsilon_r = 1 - \frac{\omega_{pe}^2}{\omega^2} + i\frac{\omega_{pe}^2}{\omega^3\tau} \quad (15)$$

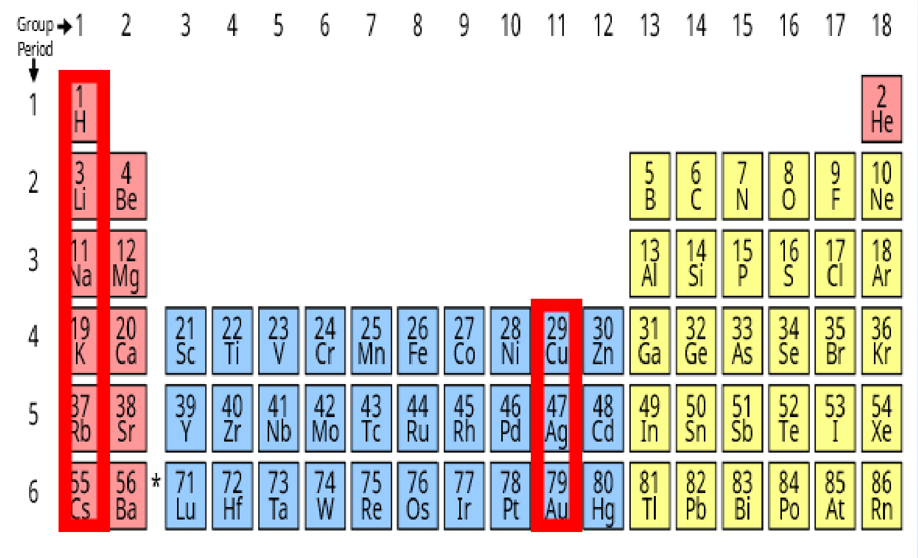
➔index n is function of

–Electron density n_e

–Resistivity ρ,

–Frequency ω

$$n = \frac{n_e^2 e^4}{\varepsilon_0 m_e^2} * \rho * \frac{1}{2k\omega^3} \quad (16)$$



n is common refractive index

k is extinction coefficient

e: is electron charge

m_e is electron mass

n_e: is electron density

ε_0: is dielectric Constance in vacuum

ρ: is resistivity

Develop a method for index calculation with two factors

- **Further simplification by an assumption 4: $\omega_{pe}^2 \gg \omega^2$**
  - valid for wavelength > 0.6 um
  - ε_r can be simplified as Eq. 17, then substitute Eq. 18 into Eq. 16

$$\varepsilon_r = -\frac{\omega_{pe}^2}{\omega^2} + i\frac{\omega_{pe}^2}{\omega^3\tau} \quad (17)$$

$$k = \sqrt{|\varepsilon_1|} = \sqrt{\frac{\omega_{pe}^2}{\omega^2}} = \frac{\sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}}}{\omega} \quad (18)$$

- **Ratio ➔cancel out most factors in index calculation**

$$\text{silver index } n_{Ag} = \frac{n_{e-Ag}^{1.5} e^3}{2\sqrt{\varepsilon_0} m_e^{1.5} \omega^2} * \rho_{Ag} \quad (19)$$

$$\text{alloy index } n_{Alloy} = \frac{n_{e-Alloy}^{1.5} e^3}{2\sqrt{\varepsilon_0} m_e^{1.5} \omega^2} * \rho_{alloy} \quad (20)$$

Index ratio

$$\frac{n_{alloy}}{n_{Ag}} = \frac{n_{e-alloy}^{3/2} * \rho_{alloy}}{n_{e-Ag}^{3/2} * \rho_{Ag}} \quad (21)$$

n_{Ag} : is silver index
n_{Alloy}: is alloy index
ρ_{Ag} : is silver resistivity
ρ_{alloy}: is alloy resistivity
n_{e-ag}: is silver electron density
$n_{e-alloy}$: is alloy electron density

only dependent on two factors n_e and ρ, (free electron density and resistivity), **with all other factors being cancelled out: (Assumption 5)**

- **Can experiments be valid for these two factors? Yes, under special conditions**
  - The Ag and AgZn alloy with low Zn concentration (<10%): The alloy co-sputter deposition conditions nearly identical to Ag's condition, except the alloy having an additional tiny Zinc co-sputtering power.

Derive thin film alloy refractive index calculation

- The alloy index can be calculated by n_e and ρ (eq. 21)
- Electron densities n_e of alloys have 2 possibilities
  - Zn atoms contributes 0 free electrons;

Alloy Index $$n_{alloy} = (1 - Zn\%)^{3/2} * \frac{\rho_{alloy}}{\rho_{Ag}} * n_{Ag} \quad (23)$$

  - Each Zn atom contributes 2 free electrons;

Alloy Index $$n_{alloy} = (1 + 1.24Zn\%)^{3/2} * \frac{\rho_{alloy}}{\rho_{Ag}} * n_{Ag} \quad (25)$$

- Experiments can tell which is the correct one
- The alloy index can be accurately predicted if Ag index, Ag-Alloy resistivity and concentration are known

electron density calculation

Alloy electron density $n_{e\_alloy} = (1 - Zn\%) n_{e\_Ag}$

Alloy electron density:

$$n_{e\_alloy} = (1 - Zn\%) n_{e\_Ag} + 2 * Zn\% * n_{e\_Zn}$$
$$= (1 - Zn\%)\, n_{e\_Ag} + 2 * Zn\% \left(\frac{7.13}{10.49} \frac{107.87}{65.38} n_{e\_Ag}\right)$$

n_{e_Zn} is transferred to n_{e_Ag} by the molecular weight and density conversion

Where Zn% is the volume percentage of Zn in the alloy

Silver molecular weight: 107.87 u

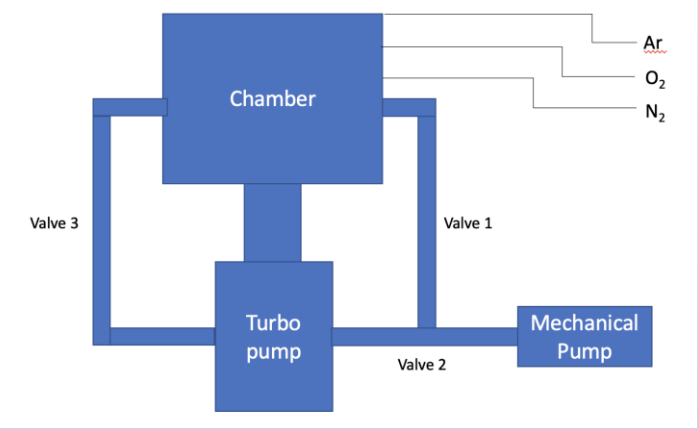
Zinc molecular weight: 65.38 u

Silver density: 10.49 g/cm^3

Zinc density: 7.13 g/cm^3

Experiment Setup

- PVD
  - Background vacuum: 2x10^{-7} torr
  - Ag and Zn target materials are 99.99%
  - Co-sputter to generate Ag Zn alloy
  - Pulsed DC (40kHz) power supply
- UV-VIS-IR Spectrometer (Shimadzu 3700)
  - 300-2500 nm spectra
  - Double beams, 3 sensors
  - Error bar is 0.2%
- Spectroscopic Ellipsometer (Woollam VASE)
  - 300-1700 nm
  - 3 measurement parameter (Delta, Psi, transmission)
  - Thickness accuracy 0.1 nm
- Four Point Probe
  - Accuracy 0. 04 ohm



Zn contributes free electrons in alloy AgZn properties or not?

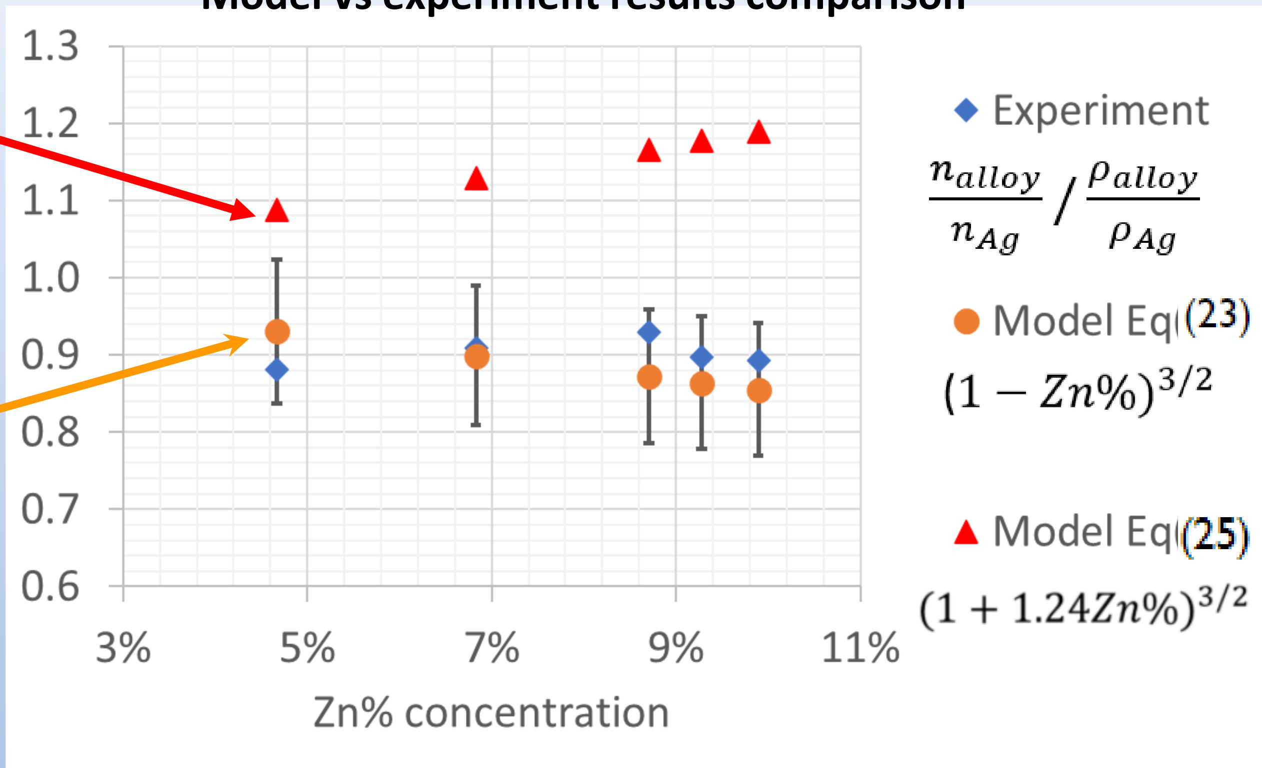
- **If each Zn atom contributes 2 free electrons in alloy properties**

$$\frac{n_{alloy}}{n_{Ag}} / \frac{\rho_{alloy}}{\rho_{Ag}} = (1 + 1.24Zn\%)^{3/2} \quad (25)$$

- **If each Zn atom contributes 0 free electrons in alloy properties**

$$\frac{n_{alloy}}{n_{Ag}} / \frac{\rho_{alloy}}{\rho_{Ag}} = (1 - Zn\%)^{3/2} \quad (23)$$

Model vs experiment results comparison



- **In conclusion, Zn contributes no free electrons**
- Error bar discussion. <±12%
  - Calculated from the sum of all standard deviations of measurements of ρ ratios <5%
  - plus the deposition n_{Ag} and n_{alloy} ratio variation of <7%,

Runsheet Summary

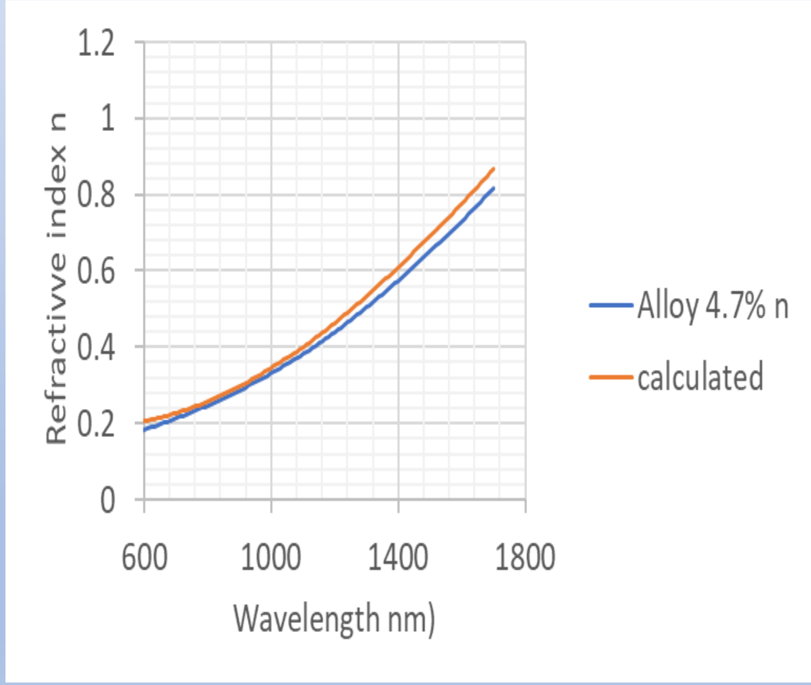
run #	Zinc power	Ag power	pressure (mT)	Ar flow (sccm)	Time Sec	thickness (nm)	Dep Rate (nm/s)	average Rs (ohm)	SteEV	1sigma	Resistivity (ohm*m)	Zn% in volume	alloy electron density (/m3)	collision time τ (s)	wavelength λ for (ωτ)^2>>1 (nm)	plasma frequency (Hz)	wavelength λ (nm) for (ωpe/ω)^2 >>1
D71-3		100w	2.5	360	70	26.4	0.38	1.4	2.5%	1.9%	3.6E-08	0	5.80E+28	1.71E-14	1.02E+04	1.36E+16	4.38E+02
D71-7	6w	100W	2.5	360	70	29.1	0.42	3.8	4.5%	1.2%	1.1E-07	9.3%	5.26E+28	6.09E-15	3.63E+03	1.29E+16	4.60E+02
D72-1		150W	2.5	360	60	34.1	0.57	1.0	2.2%	2.2%	3.4E-08	0	5.80E+28	1.80E-14	1.07E+04	1.36E+16	4.38E+02
D72-3	6w	150W	2.5	360	60	36.6	0.61	2.7	2.8%	1.0%	9.9E-08	6.8%	5.40E+28	6.65E-15	3.96E+03	1.31E+16	4.54E+02
D72-5		200W	2.5	360	45	34.7	0.77	1.1	1.9%	1.8%	3.7E-08	0	5.80E+28	1.66E-14	9.91E+03	1.36E+16	4.38E+02
D72-7	6w	200W	2.5	360	45	36.4	0.81	2.2	2.0%	0.9%	7.9E-08	4.7%	5.53E+28	8.10E-15	4.82E+03	1.33E+16	4.49E+02
D73-1		100W	2.5	360	90	34.6	0.38	1.0	3.0%	3.0%	3.5E-08	0	5.80E+28	1.77E-14	1.05E+04	1.36E+16	4.38E+02
D73-5	6w	100W	2.5	360	90	37.9	0.42	2.9	2.7%	0.9%	1.1E-07	8.7%	5.29E+28	6.19E-15	3.69E+03	1.30E+16	4.59E+02
D73-7	6w	100W	2.5	360	90	38.4	0.43	2.8	4.4%	1.5%	1.1E-07	9.9%	5.23E+28	6.26E-15	3.73E+03	1.29E+16	4.62E+02

- 3 different Zn% of AgZn alloy were studied by co-sputter method,
- To meet our assumptions, we need the wavelength to be at least greater than 600nm and smaller than 3000nm:
  - Assumption 3: $\omega^2\tau^2 \gg 1$; Valid for wavelength < $3\mu m$
  - Assumption 4: $\boldsymbol{\omega_{pe}^2} \gg \boldsymbol{\omega^2}$: valid for wavelength > 0.6 um

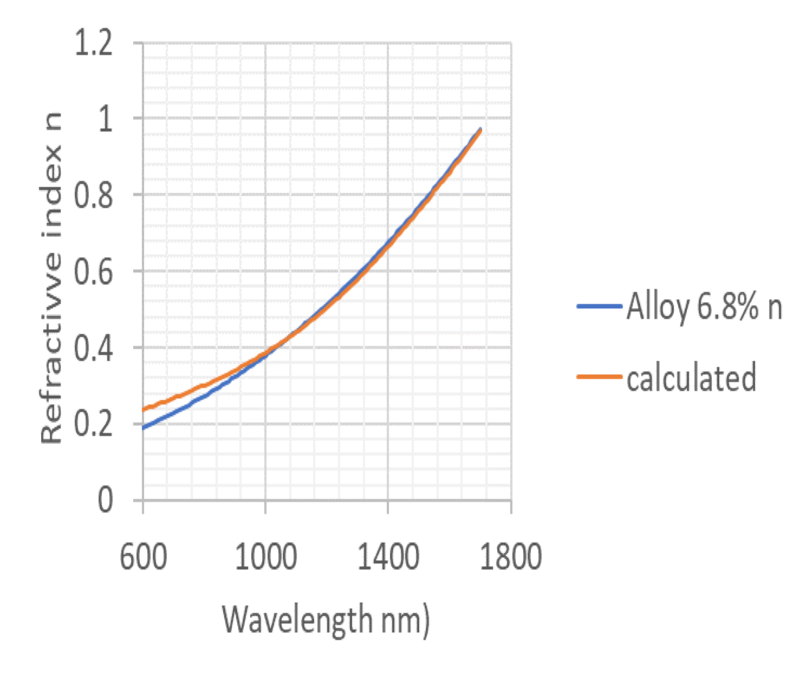
Alloy index model calculation vs experiment measurements

Alloy Index : $n_{alloy} = (1 - Zn\%)^{3/2} * \frac{\rho_{alloy}}{\rho_{Ag}} * n_{Ag}$ **(26)**

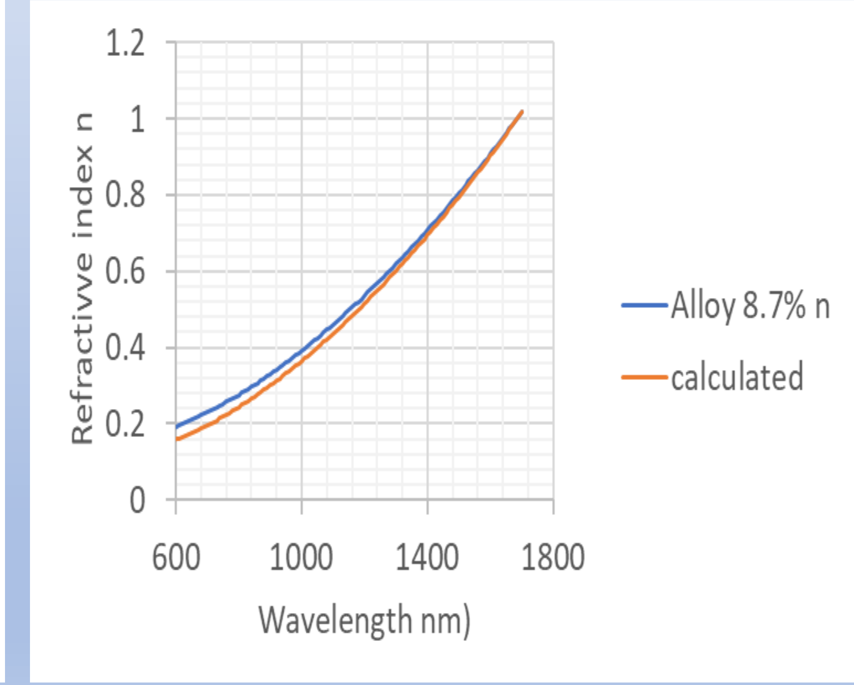
AgZn (Zn 4.7%)



AgZn (Zn 6.8%)



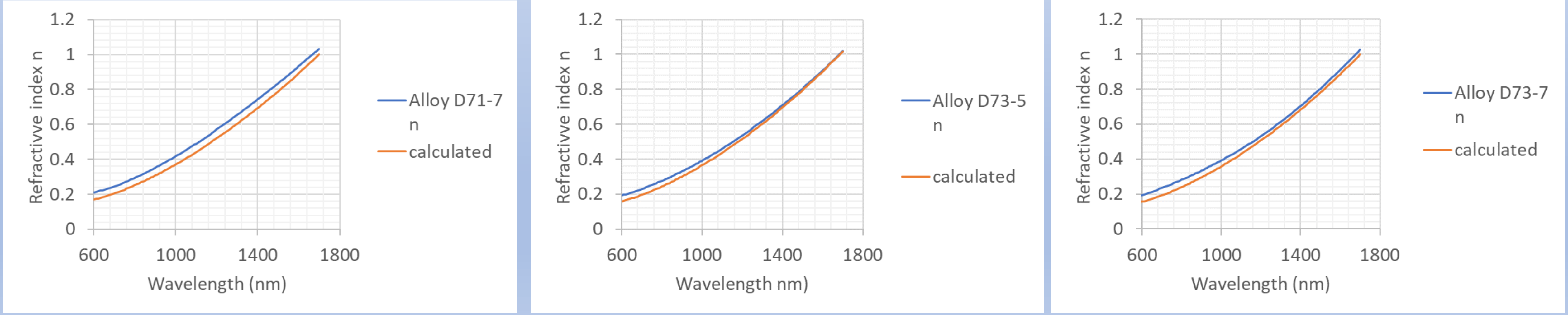
AgZn (Zn 8.7%)



The model calculations and the experiment results match up well

Repeatability study:

- Indexes ratio variation from three model calculation showed ~7% standard deviation in average of the spectra.
  - Two Silver depositions of 100W with <4% index variation
  - Three Alloy depositions of 100W Ag + 6 W Zn with <3% index variation



Repeated Silver alloy index of 100wAg + 6W Zn and the calculation from the theory eq. (26)

Conclusions

- We theoretically derived a refractive index calculation that depends only on two parameters which canceled out other factors.

$$\frac{n_{alloy}}{n_{Ag}} = \frac{n_{e-alloy}^{3/2} * \rho_{alloy}}{n_{e-Ag}^{3/2} * \rho_{Ag}}$$

  - Valid experimental conditions were confirmed between 0.6 μm and 3 μm

- Alloy index with concentration relationship was derived:

$$n_{alloy} = (1 - Zn\%)^{3/2} * \frac{\rho_{alloy}}{\rho_{Ag}} * n_{Ag}$$

  - Theory and experiments agree within error bar
  - Experimentally confirmed that Zn contributes no free electrons in alloy AgZn film properties in this study.

Future study on why Zn does not contribute free electron in AgZn alloy?

- This study indicated that Zn does not contribute free electron in AgZn alloy.

- Literature report AgGe with alloy concentration 26%-37%, the 2nd element Ge contribute free electrons

- However, there are literature of AgFe with 1%, AlCu(0.5%-1.5%) ….alloy free electrons are lower than the pure silver concentration, which means the 2nd element is likely not contribute free electron.

- Our hypothesis is: at very low concentration of alloy element in a highly conducting metal silver, the electrons from the 2nd element is localized and is not able to contribute any free electrons to the conducting current.

- Any suggestion?

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