

Investigation of hydrogenated silicon nitride thin films

Report on Phd activity of 2019/2020-1 semester

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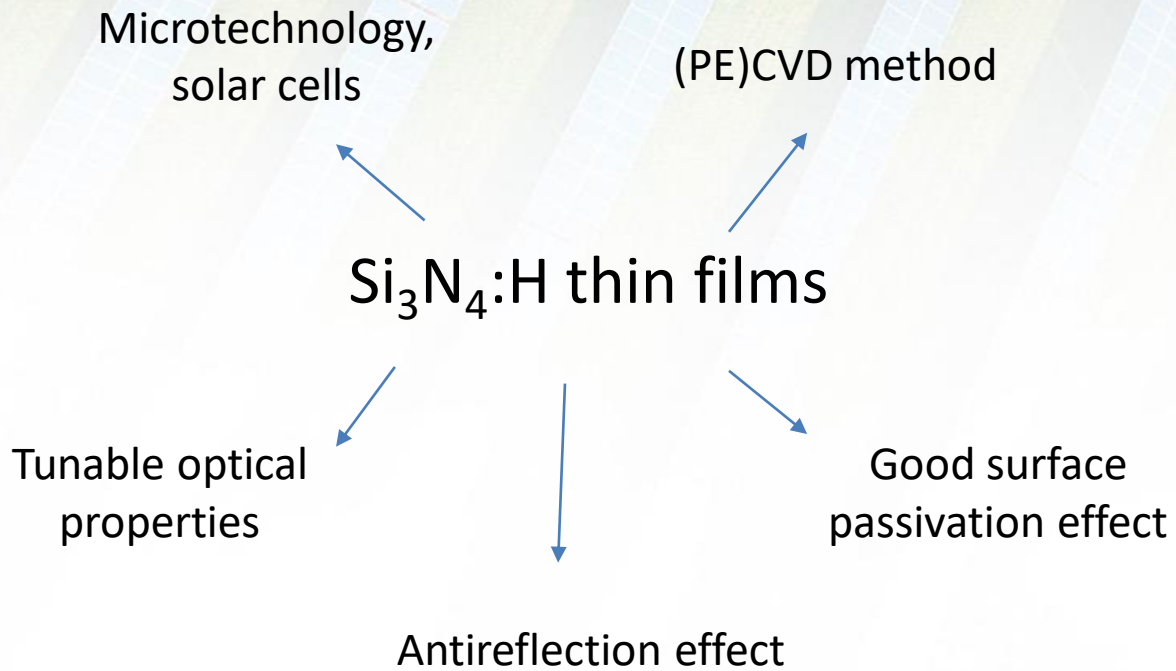


See what's possible™

Motivation

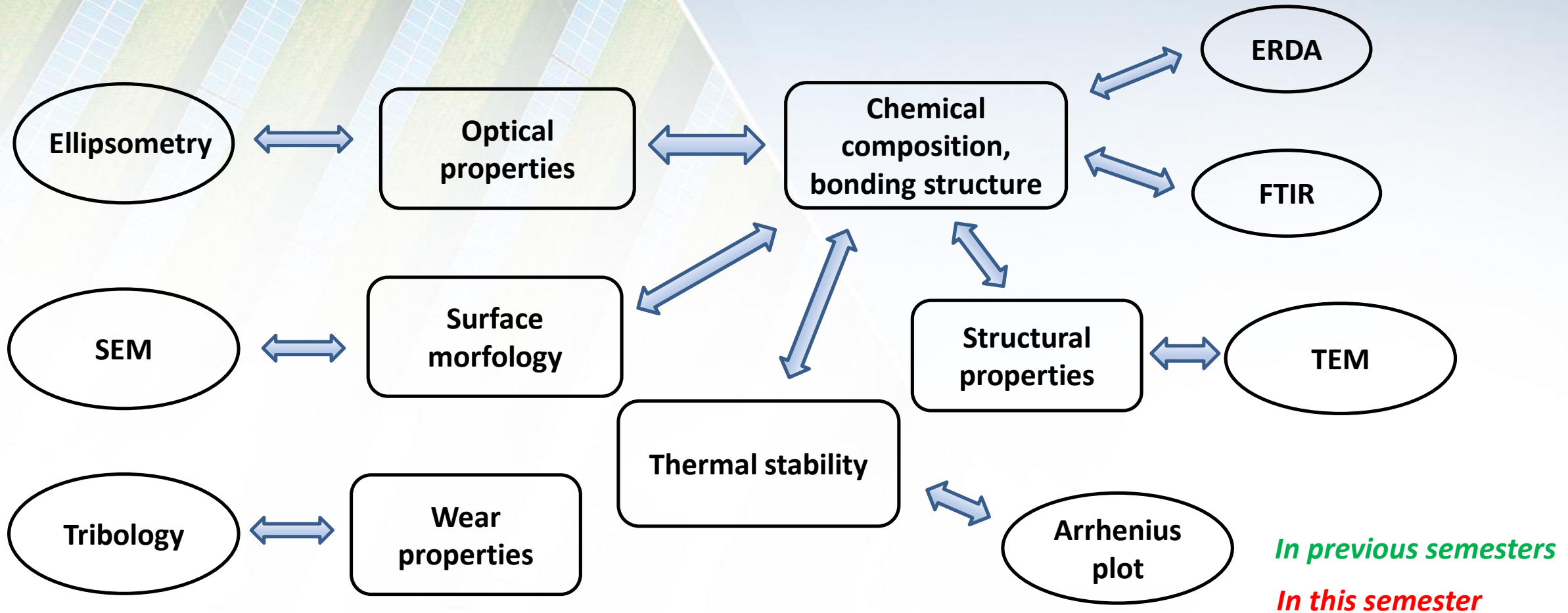
Radio Frequency (RF) sputtering as alternative method

- Cost saving method
- Easy to scale up
- Low deposition temperature
- Avoid of toxic gases



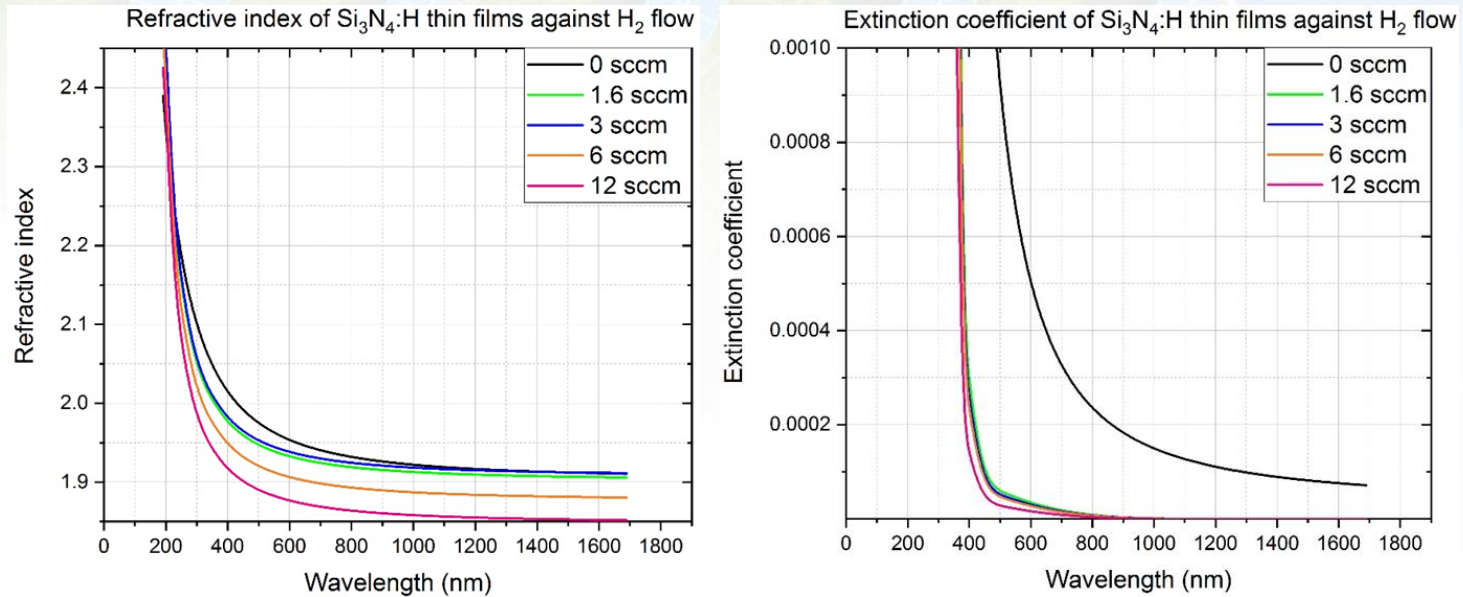
ADVANTAGE

Overview of performed measurements



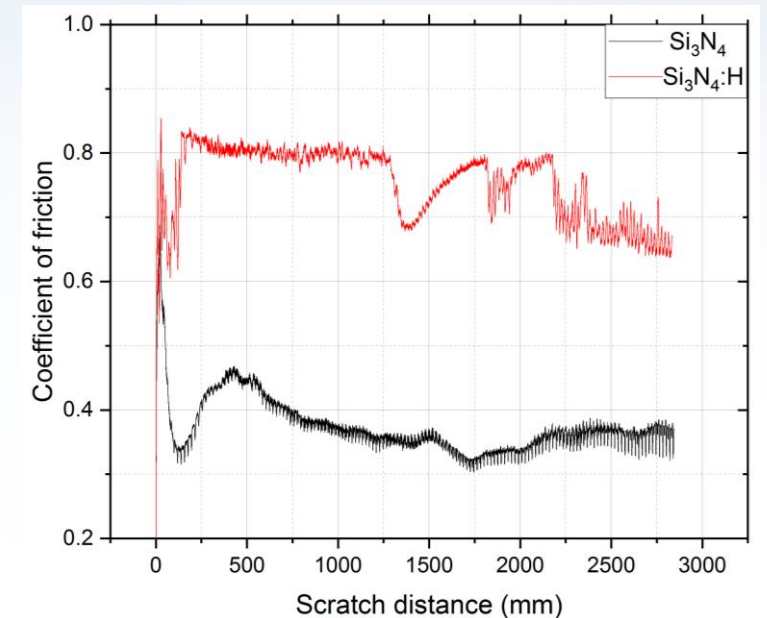
Previous results 1/2

Optical properties



Refractive index and extinction coefficient are decreased while hydrogen flow is increased

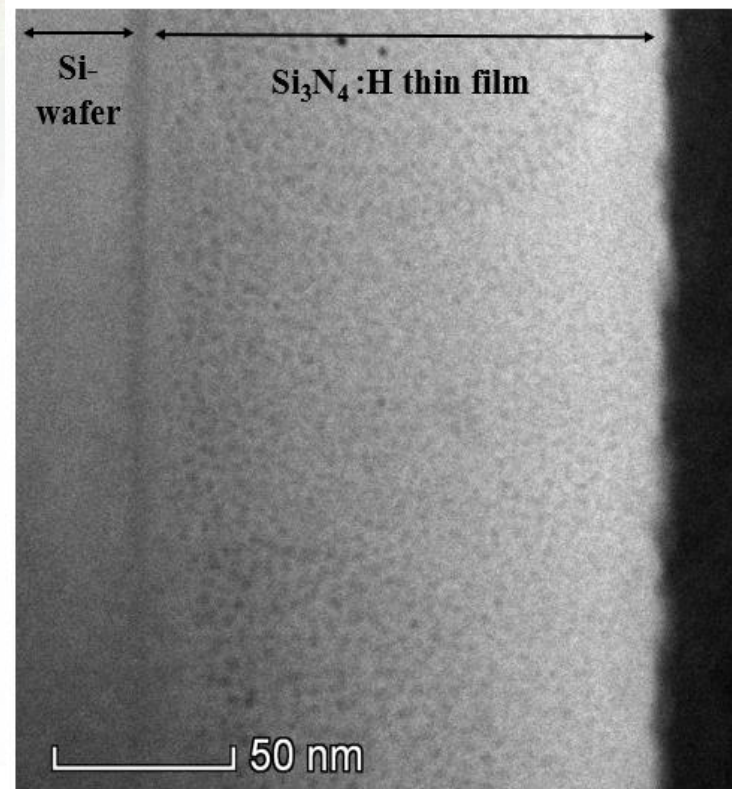
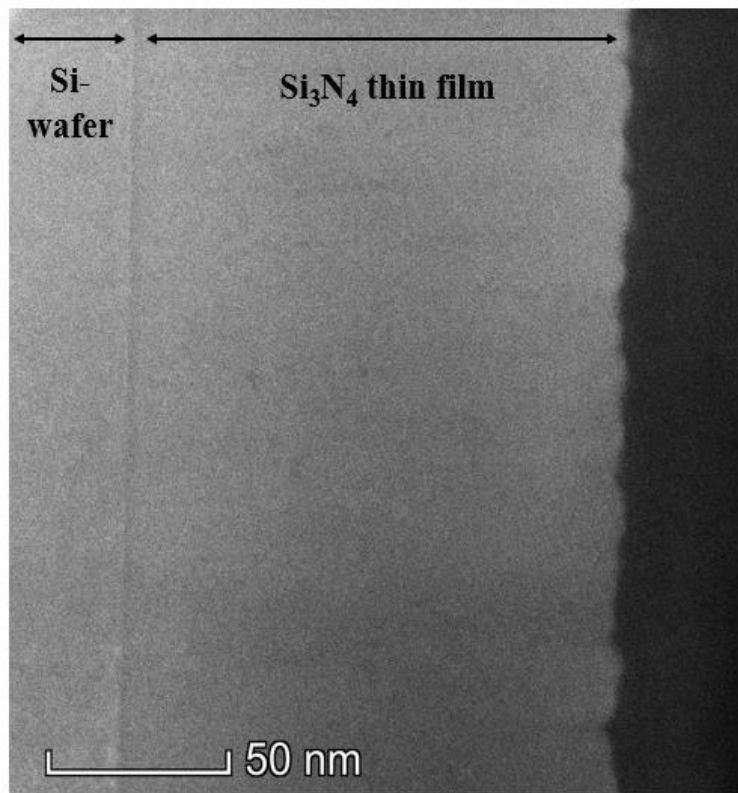
Wear properties



Presence of hydrogen increases the coefficient of friction of the thin film

Previous results 2/2

Structural properties – TEM HAADF pictures

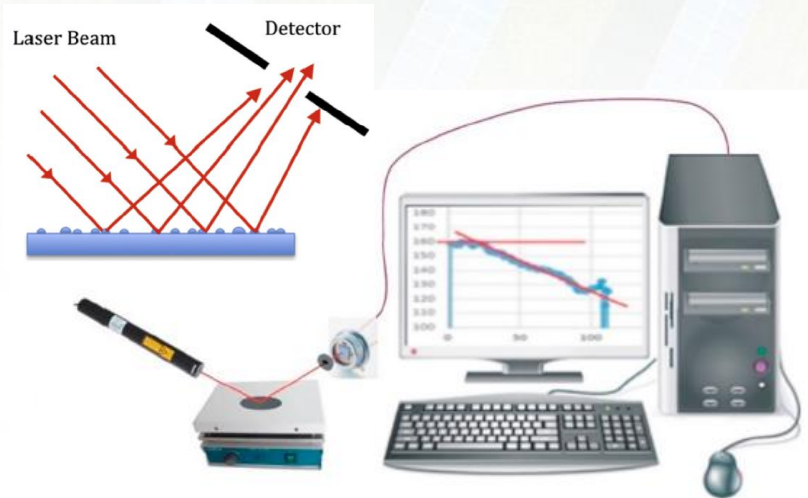


The films are amorphous, no crystalline phase is visible

Hydrogenated layer (right) is more porous than hydrogen free one (left)

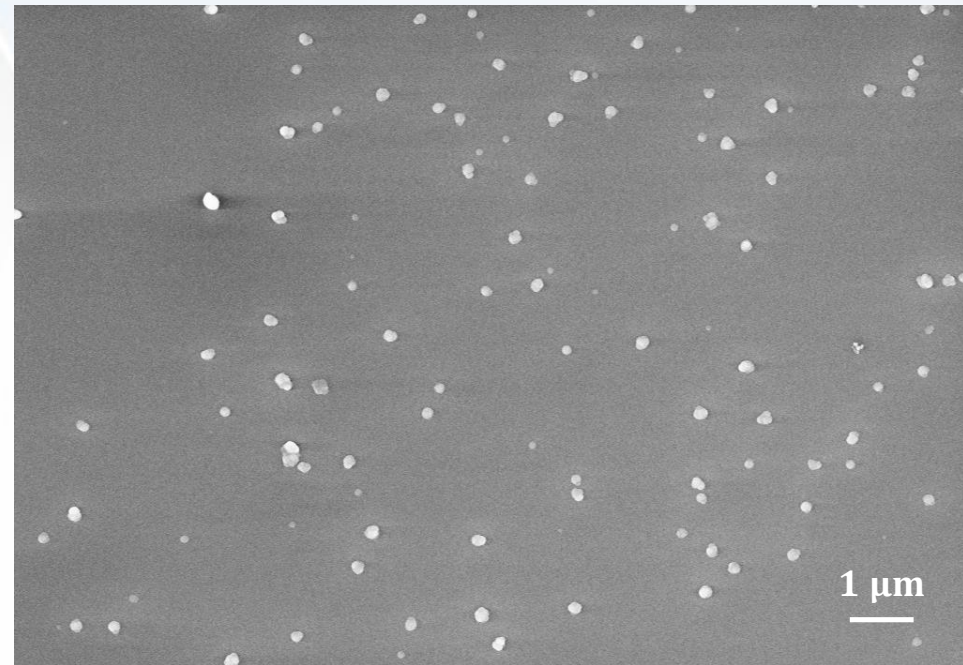
Annealing

H₂ release from Si₃N₄:H thin films upon annealing

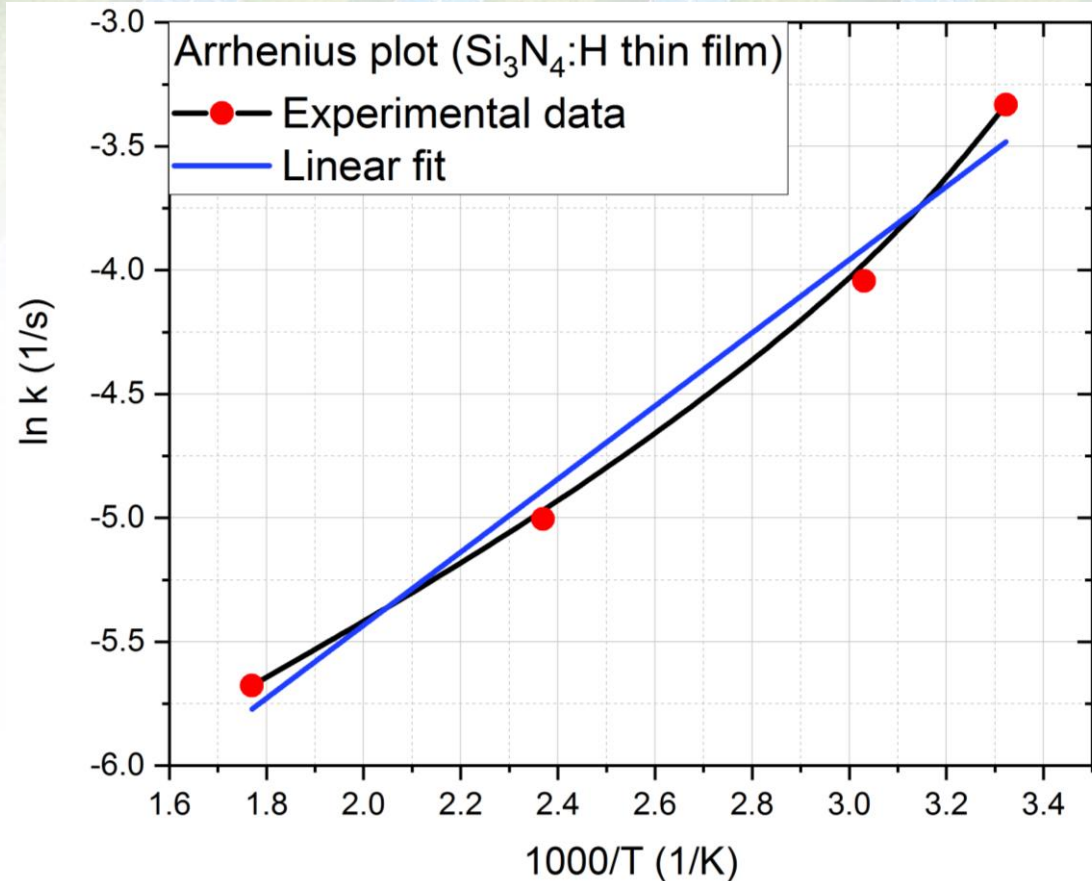


Optical method for determining the onset of the phenomena

SEM picture of surface of annealed Si₃N₄:H thin film



Arrhenius-method



Arrhenius-equation

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad k = \frac{1}{t}$$

$$\ln \frac{1}{t} = \ln A - \frac{E_a}{RT}$$

$$E_a \approx 12.26 \frac{\text{kJ}}{\text{mol}}$$

Bond dissociation energies:

$$H - N: 314 \frac{\text{kJ}}{\text{mol}}$$

$$H - Si: 298 \frac{\text{kJ}}{\text{mol}}$$

k: rate constant

A: pre exponential factor

R: universal gas constant

T: absolute temperature

t: elapsed time

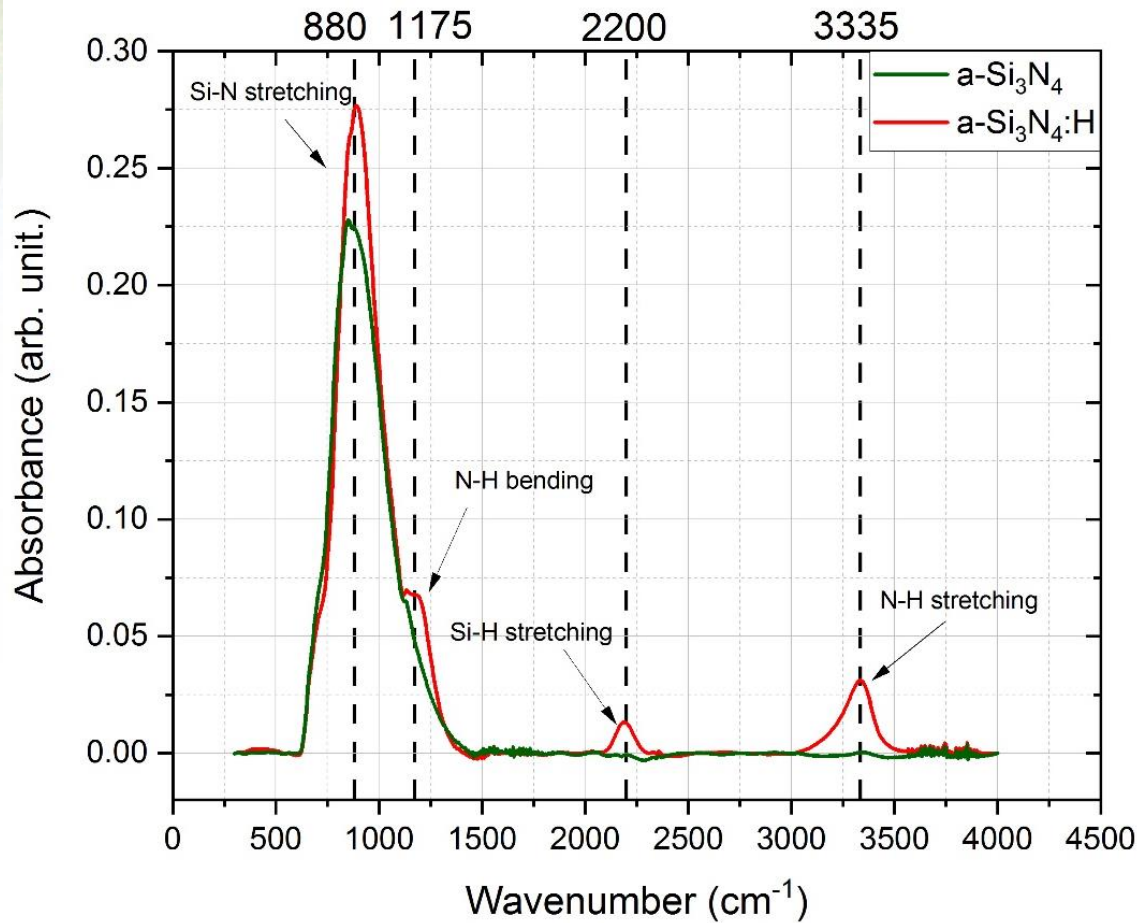
Ea: activation energy

Constant

Measured

Questionable

Infrared spectroscopy



Quantitative analysis



Lanford-Rand-method

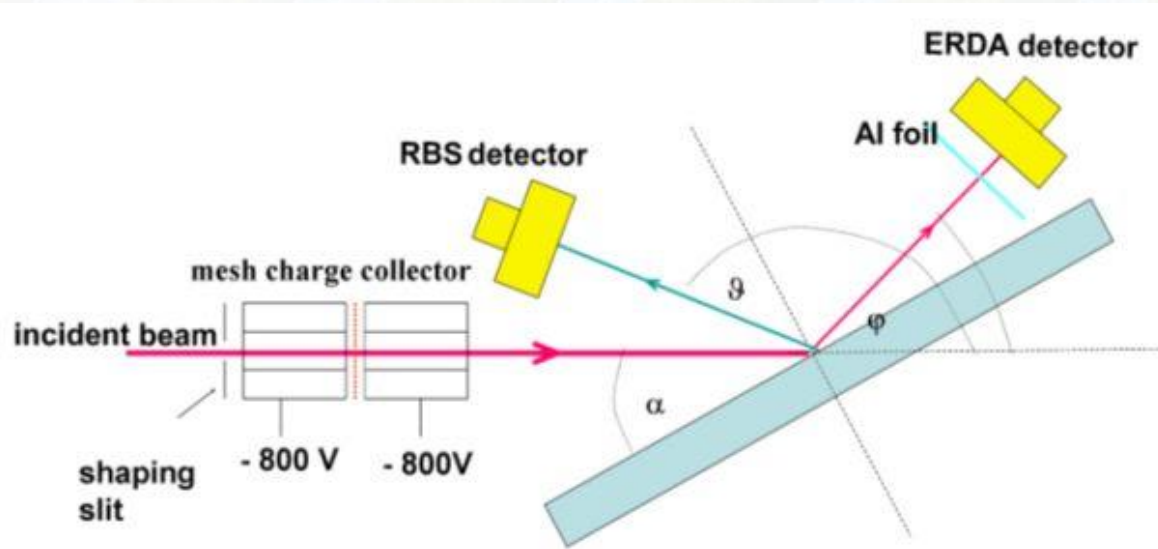
$$C_{Y-H} = \frac{A_{Y-H}}{\ln 10 \cdot \sigma_{Y-H}}$$

N-H	Si-H
$3.49 \cdot 10^{20} \frac{1}{\text{cm}^3}$	$0.61 \cdot 10^{20} \frac{1}{\text{cm}^3}$

This method is only sensitive for **bound** hydrogen

FTIR vs. ERDA

Schematic Overview of Elastic Recoil Detection Analysis



Hydrogen concentration

Bound – FTIR	Total – ERDA
$4.1 \cdot 10^{20} \frac{\text{atoms}}{\text{cm}^3}$	$9.6 \cdot 10^{21} \frac{\text{atoms}}{\text{cm}^3}$



Less than 5% of total hydrogen atoms are bonded to silicon or nitrogen atoms



Hydrogen mainly exists in the film in *molecular* form

Conclusions

Hydrogen is in the film
dominantly in molecular form

Increased porosity
and decreased
density (TEM)

Hydrogen releases at
low temperature

Blistering of the
sample surface
(SEM)

Low activation
energy (Arrhenius-
method)



Subjects, publications

- Subjects:
 - Mechanical properties of engineering ceramics (Dr. Ján Dusza)
 - Material structure and fracture mechanism of engineering ceramics (Dr. Ján Dusza)
- Publications:
 - Writing publications is in progress about the presented results and a review on hydrogenated silicon nitride thin films



Presentations

Poster presentation XVI. Conference and Exhibition of the European Ceramic Society

Oral presentation 2nd Fine Ceramic Day Science Society of Silicate Industry

HYDROGEN EFFECT ON THE OPTICAL AND MECHANICAL PROPERTIES OF Si_3N_4 THIN FILMS
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Introduction
Ceramic hydrogenated silicon nitride thin films are of great interest for their wide range of applications in microelectronics. The main reason for this is their high thermal stability and low thermal expansion coefficient. The hydrogenation process can be used to modify the optical and mechanical properties of the films. In this work, the effect of hydrogenation on the optical and mechanical properties of Si_3N_4 thin films is investigated. The samples were prepared by PECVD and hydrogenated in a hydrogen atmosphere at different temperatures. The optical properties were measured by ellipsometry and the mechanical properties were measured by nanoindentation.

Ellipsometry
Ellipsometry is a non-destructive optical technique that measures the change in polarization of light upon reflection from a surface. It is used to determine the thickness and refractive index of thin films. In this work, ellipsometry was used to measure the optical properties of the hydrogenated Si_3N_4 thin films. The results show that the refractive index of the films increases with increasing hydrogenation temperature.

Optical properties
The optical properties of the hydrogenated Si_3N_4 thin films were measured by ellipsometry. The results show that the refractive index of the films increases with increasing hydrogenation temperature. This is due to the formation of hydrogenated silicon nitride (Si₃N₄H_x) in the films. The optical properties of the films were also measured by UV-Vis spectroscopy. The results show that the absorption coefficient of the films increases with increasing hydrogenation temperature.

TEM
Transmission electron microscopy (TEM) was used to investigate the microstructure of the hydrogenated Si_3N_4 thin films. The results show that the films consist of a network of nanoscale hydrogenated silicon nitride (Si₃N₄H_x) particles embedded in a matrix of silicon nitride (Si₃N₄). The size of the Si₃N₄H_x particles increases with increasing hydrogenation temperature.

FTIR results
Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical structure of the hydrogenated Si_3N_4 thin films. The results show that the films contain Si-N and Si-H bonds. The Si-H bond is characteristic of hydrogenated silicon nitride (Si₃N₄H_x). The intensity of the Si-H bond increases with increasing hydrogenation temperature.

Conclusion
The results of this work show that the optical and mechanical properties of Si_3N_4 thin films are affected by hydrogenation. The refractive index of the films increases with increasing hydrogenation temperature. This is due to the formation of hydrogenated silicon nitride (Si₃N₄H_x) in the films. The optical properties of the films were also measured by UV-Vis spectroscopy. The results show that the absorption coefficient of the films increases with increasing hydrogenation temperature. TEM and FTIR spectroscopy were used to investigate the microstructure and chemical structure of the hydrogenated Si_3N_4 thin films. The results show that the films consist of a network of nanoscale hydrogenated silicon nitride (Si₃N₄H_x) particles embedded in a matrix of silicon nitride (Si₃N₄). The size of the Si₃N₄H_x particles increases with increasing hydrogenation temperature. FTIR spectroscopy was used to investigate the chemical structure of the hydrogenated Si_3N_4 thin films. The results show that the films contain Si-N and Si-H bonds. The Si-H bond is characteristic of hydrogenated silicon nitride (Si₃N₄H_x). The intensity of the Si-H bond increases with increasing hydrogenation temperature.



Plans for the next semester

- Preparation of first publication with IF
- Explain the results with theoretical model
- Investigate the influence of the process parameters on the ratio of bound/unbound hydrogen content in the film



Acknowledgement

- Dr. Csaba Balázs and Dr. Katalin Balazsi¹ (supervisors)
- Dr. Lovics Riku¹ and Dr. Miklós Serényi² (RF-sputtering)
- Dr. Judith Mihály³ (FTIR-measurements)
- Dr. Péter Petrik² (SE-measurements)
- Dr. Zsolt Zolnai⁴ (ERDA-measurements)
- Tamás Zagya¹ (Tribology-measurements)



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Thank you for your attention!

Thank You