SUMMER SCHOOL ON

BASICS AND APPLICATIONS OF NANOLITHOGRAPHY

ORGANIZERS

*SORAYA SANGIAO: *JOSÉ MARÍA DE TERESA:

***GROUP WEBPAGE:**

sangiao@unizar.es deteresa@unizar.es http://nanofab-deteresa.com

(under construction)

http://nanofab.unizar.es





UNIVERSITY OF ZARAGOZA

SUMMER SCHOOLS IN JACA









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ARAGON: A TERRITORY LINKED TO ARTS AND SCIENCE



***Miguel Servet** (1509-1553): discoverer of the lung blood circulation. Dead in the bonfire in Geneva.

*Santiago Ramón y Cajal (1852-1934): discoverer of the nerve cells connections. Nobel Prize in Medicine in 1906. *Miguel Catalán (1894-1957): discoverer of the multiplets, the splitting of the atomic energy levels.

FRANCISCO DE GOYA (aragonese painter, 1746-1828)

BALTASAR GRACIAN (aragonese writer, 1601-1658)





audacia en todo lo que hagas"

"Put a gram of audacity in all

you do"

"Pon siempre un gramo de



*Student reward: ONE FREE BEER on TUESDAY at 8pm for all students who asked at least TWO QUESTIONS per day

SUMMER SCHOOL ON

BASICS AND APPLICATIONS OF NANOLITHOGRAPHY

QU'EST-QUE C'EST NANOLITO?



<u>NANOLITO</u>: Spanish network of excellence on Nanolithography, funded by the Ministry of Science (started in 2007)

> Coordinating node: Zaragoza (INA, ICMA)

Other nodes: Madrid (ISOM, UCM, ICMM, IMDEA) Barcelona (CNM, UB, ICN2) San Sebastián (Nanogune) Oviedo (U. Oviedo) Eibar (Tekniker)

Webpage: <u>www.unizar.es/nanolito</u> Twitter: @RedNanolito



Cursos de verano Universidad de Zaragoza

Vicerrectorado de Proyección Cultural y Social



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SAN SEBASTIAN-2016





oct

CHECK OUT MORE PHOTOS

Nano 2D

SALAMANCA-2017



in nanolithography

i dea

NANOLITO 2017 25-26 January (Salamanca)



NANODEVICES BASED ON GRAPHENE AND 2D MATERIALS

Introduction to Nanolithography



NANOTECHNOLOGY EXISTS IN NATURE

From micro to nano contacts in biological attachment devices

Eduard Arzt**, Stanislav Gorb*§, and Ralph Spolenak*

*Max Planck Institute for Metals Research, Heisenbergstrase 3, 70569 Stuttgart, Germany; and ⁵Biological Microtribology Group, Max Planck Institute of Developmental Biology, Spemannstrase 35, 72076 Tübingen, Germany





CAN WE CREATE ARTIFICIAL PROCESSES TO PATTERN MATERIALS AND DEVICES TO THE NANOSCALE? YES!

TRANSISTORS IN MICROPROCESSORS: current node= 14 nm



MEMORIES AND READING HEADS BASED ON NANOMAGNETIC ELEMENTS

[Ferro/metal]_n

20 nm

103 TMR head/CPP-GMR head Perpendicular recording 10² Demonstration Spin-valve 10 GMR head (Gbit/in²) 100 IR head density 10 10-2 Areal nductive thin film head 10-3 Ferrite head 10 Coating disk Sputtered metal disk 10 1970 1980 2000 2010 1990 Year



PHYSICAL PHENOMENA CAN ALSO CHANGE AT THOSE DIMENSIONS!



In Mesoscopic Physics, some dimension of the material/device is comparable or smaller than some relevant length, such as the mean free path in metals, the exchange length and the spin diffusion length in magnetic materials, the coherence length and the magnetic field penetration length in superconductors...Besides, fluctuations become more important.

When dimensions are small enough, the discretization of the energy states becomes relevant and the system needs to be described by means of Quantum Physics. $\Delta E_{\rm K}/K_{\rm B}T\approx 1$ (at RT, $K_{\rm B}T=25$ meV and $\Delta E_{\rm K}=25$ meV, typically for L<10 nm)

INTRODUCTION TO NANOLITHOGRAPHY (I)

TOP-DOWN APPROACH

Thin-film growth technology + Lithography techniques If lateral dimensions are smaller than 1 μm, we talk about "nanolithography"



Thin-film growth technology

Physical vapour deposition (sputtering, evaporation), chemical vapour deposition, liquid-phase deposition (electrodeposition, spin coating), Langmuir-**Blodgett...**

Lithography techniques Optical lithography, electron beam lithography, focused ion beam, scanning probe lithography, nanoimprinting, nanostencil,...







INTRODUCTION TO NANOLITHOGRAPHY (II)

⇒ THE LITHOGRAPHY IS THE SET OF TECHNIQUES ALLOWING THE TRANSFER OF PATTERNS TO A SAMPLE. THE TYPICAL MINIMUM SIZE IN THE TRANSFERED PATTERNS IS MICROMETRIC OR NANOMETRIC.



INTRODUCTION TO NANOLITHOGRAPHY (III)

 10⁻⁴ m
 10⁻⁵ m
 10⁻⁶ m
 10⁻⁷ m
 10⁻⁸ m

 Micrometric range (10⁻³-10⁻⁶ m)
 Nanometric range (10⁻⁶-10⁻⁹ m)

 Optical lithography
 Electron-beam lithography (EBL, FEBID)
 Ion-beam lithography (FIB, FIBID)
 Nanoimprinting
 Scanning Probe Lithography (SPL-AFM)

⇒ Besides resolution, other important aspects to consider are: speed, cost, reproducibility, possibility to develop complex patterns, accessibility to the technique...

INTRODUCTION TO NANOLITHOGRAPHY (IV)

⇒ LITHOGRAPHY PROCESSES SHOULD BE PERFORMED IN CLEAN ROOMS

-A Clean Room is a space with controlled environmental conditions, keeping low levels of contamination (dust, particles, microbes...)

-In a Clean Room the following parameters are controlled:

-Number and dimensions of the particles present in the air

- -Temperature
- -Humidity
- -Differential pressure and flow of air
- -Illumination
- -Electrostatic protection

ISO RULE 14644



APPLICATIONS AREAS: -MICRO- AND NANO-ELECTRONICS -FARMACEUTICS -FOOD INDUSTRY -MICROSYSTEMS -HOSPITALS AND CLINICS -PLASTICS AND CHEMISTRY INDUSTRY

INTRODUCTION TO NANOLITHOGRAPHY (V)

\Rightarrow HOW CAN WE KEEP A ROOM CLEAN?



INTRODUCTION TO NANOLITHOGRAPHY (VI)

FFU (filter/fan unit)

\Rightarrow HOW CAN WE KEEP A ROOM CLEAN?

-HEPA (High-efficiency particulate air) FILTER: 99.97% -99.99% (0.3μm)

-ULPA (Ultra high-efficiency particulate air) FILTER :99.9995% (0.12µm)



Class		FED STD 209E					
	≥0.1 µm	≥0.2 µm	≥0.3 µm	≥0.5 µm	≥1 µm	≥5 µm	equivalent
ISO 1	10	2.37	1.02	0.35	0.083	0.0029	
ISO 2	100	23.7	10.2	3.5	0.83	0.029	
ISO 3	1,000	237	102	35	8.3	0.29	Class 1
ISO 4	10,000	2,370	1,020	352	83	2.9	Class 10
ISO 5	100,000	23,700	10,200	3,520	832	29	Class 100
ISO 6	1.0 × 10 ⁶	237,000	102,000	35,200	8,320	293	Class 1,000
ISO 7	1.0 × 10 ⁷	2.37 × 10 ⁶	1,020,000	352,000	83,200	2,930	Class 10,000
ISO 8	1.0 × 10 ⁸	2.37×10^{7}	1.02×10^{7}	3,520,000	832,000	29,300	Class 100,000
ISO 9	1.0 × 10 ⁹	2.37 × 10 ⁸	1.02 × 10 ⁸	35,200,000	8,320,000	293,000	Room air

Class	Air flow speed	Renovations per hour	Percentage of ceiling covered
10000	0.05-0.08 m/s	60-90	15-20%
1000	0.13-0.2 m/s	150-240	25-40%
100	0.2-0.4 m/s	240-280	35-70%



Optical Lithography



TECHNOLOGICAL EVOLUTION IN OPTICAL LITHOGRAPHY

UV MASK ALIGNER (lab technology)

> UV STEPPER (semicon industry, today)



EUV STEPPER (semicon industry, tomorrow)



BASIC PROCESS

- 1) GROWTH OF THE MATERIAL
- 2) BASIC LITHOGRAPHY PROCESS

TWO APPROACHES TO WORK WITH RESISTS (in optical and electron-beam lithographies)

LIFT-OFF PROCESS

- 1) BASIC LITHOGRAPHY PROCESS
- 2) GROWTH OF THE MATERIAL IN AN INTERMEDIATE STEP OF THE LITHOGRAPHY PROCESS

⇒ AN ACTUAL FULL LITHOGRAPHY PROCESS INVOLVES MANY BASIC AND LIFT-OFF PROCESSES ONE AFTER THE OTHER



OPTICAL LITHOGRAPHY MASKS



CHROMIUM MOTIFS (absorbers of the U.V. light)

QUARTZ SUBSTRATE (transparent at UV wavelenghts)







<u>RESISTS:</u> VISCOUS FLUID FORMED BY A <u>POLYMER</u>, A <u>PHOTOSENSITIVE COMPONENT</u> AND A <u>SOLVENT</u>



LIFT-OFF PROCESS (WITH POSITIVE RESIST)





WITHOUT ETCHING STEP!!

DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (I)

RESIST SPIN COATING



A subsequent soft bake (90-100°C) eliminates the solvent, improves the adhesion and avoid strains. A primer substance improves the adhesion of the resist.





DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (II)

wavelength λ (nm)

MASK ALIGNER



-By means of optical filters, the working wavelength can be selectioned

-*LAMP*: Hg (emission lines: G at 436 nm, H at 405 nm, I at 365 nm)



DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (III)



DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (IV)

STEPPERS IN SEMICON INDUSTRY



MINIMUM SIZE OF THE MOTIFS= K λ / (NA)

*<u>Throughput</u>: 200 wafers per hour

*<u>Wafer diameter:</u> up to 300 mm

*<u>Tricks</u>: immersion lens, phase-shift masks, double exposure

*Resolution:

 $0.35 \ \mu m \ (1997) \rightarrow$ $0.18 \ \mu m \ (2002) \rightarrow$ $90 \ nm \ (2007) \rightarrow$ $30 \ nm \ (2013) \rightarrow$ $10 \ nm \ (2017)$

DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (V)

STEPPERS IN SEMICON INDUSTRY

https://www.youtube.com/watch?v=ShYWUIJ2FZs

DESCRIPTION OF THE STEPS IN OPTICAL LITHOGRAPHY (VI)

ETCHING PROCESSES

-WET ETCHING: BY MEANS OF REACTIVE LIQUIDS THAT PRODUCE A SOLUBLE BY-PRODUCT

-DRY ETCHING: A VOLATILE COMPOUND IS FORMED

*PHYSICAL ETCHING: BY MEANS OF SPUTTERING AND IONIC BOMBARDEMENT (IBE) *PHYSICAL/CHEMICAL ETCHING: BY MEANS OF PLASMA, REACTIVE ION ETCHING (RIE)...



WHAT COMES NEXT?

Wavelength (nm)	Source	
436	G line of Hg lamp	
365	I line of Hg lamp	
248	KrF laser	
193	ArF laser	
157	F ₂ laser	
~10	Plasma (EUV) 🗧 🗧	
~1	X-rays, synchrotron	

PRODUCTION TO START IN 2020 TO REACH SUB-10 nm NODES

EUV LITHOGRAPHY (I)

CHANGE FROM REFRACTION OPTICS TO REFLECTION OPTICS







Difficulties:

- *Low-efficiency energetic process
- *Short lifetime of the elements
- *Suitable resists needed
- *Suitable masks needed
- *Suitable mirrors needed





TECHNOLOGICAL EVOLUTION IN OPTICAL LITHOGRAPHY



EUV IS THE NEXT STEP IN OPTICAL LITHOGRAPHY



ASML SELLS THE NEW EUV MACHINES for 100 MILLION EURO EACH COMPANIES SUCH AS INTEL AND GLOBAL FOUNDRIES TO PRODUCE 7 nm CHIPS SINCE 2020

Introduction to Nanofabrication techniques

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Outline

- Introduction:
 - Nanotechnology.
 - Length scales.
 - > Applications.
 - Nanolithography techniques.
- Optical lithography.
- Scanning Electron Microscopy (SEM).
- Electron Beam Lithography (EBL).
- Focused Electron Beam Induced Deposition (FEBID).



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Jaca, July 16th, 2018


<u>Electron microscopy</u>: science that allows us to visualize objects in magnified way by using an electron beam.

> 1924. Louis de Broglie proposed that all particles behave to an extent like waves, and have properties such as wavelength and frequency:

 $\lambda \sim h / mv$

> As a consequence, electron microscopes can have much higher resolution than optical microscopes: an electron accelerated at 25 kV has an associated wavelength of 0.008 nm.

> 1933: Manufacturing of the first Transmission Electron Microscope (TEM) by Ernst Ruska and Max Knoll.

> 1935: Developing of the concept of Scanning Electron Microscope (SEM) by Max Knoll.

I938: Manufacturing of a high resolution SEM by Manfred von Ardenne (resolution of 50 nm).



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Description of a SEM

-<u>UNDERLYING</u> CONCEPT OF EBL:

$\lambda \sim h/mv$

Which implies that electron acceleration to high speed produces short wavelengths, applicable in lithography:

-For example:

 λ = 0.008 nm at 25 kV





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Description of a SEM		Source type	Filament	Brightness	Source	Energy	Vacuum	Filament	
	EMITTER	Working principle	material	(A/cm ² /rad)	size	dispersion (eV)	level (Torr)	temperature (K)	
			Tungsten thermoionic	W	$\sim 10^5$	25 µm	2-3	10-6	~3000
			LaB ₆ thermoionic	LaB₀	$\sim 10^{6}$	10 µm	2-3	10-8	~2000-3000
	LENSES		Thermic field emission	Zr/O/W	~10 ⁸	20 nm	0.9	10-9	~1800
	BEAM DEFLECTOR		(Schottky) Cold field emission	W	~109	5 nm	0.22	10-10	Ambience



W filament



LaB₆ crystal

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Field emission







EMITTER

LENSES

BEAM DEFLECTOR



FIG. 2.8. Schematic showing the magnetic (electrostatic) field distribution for a) a simple beam deflector or alignment device energized for diagonal deflection and b) a stigmator. The optical axis is perpendicular to the plane of the page.



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Description of a SEM

SEM vs optical microscope: SEM:

Optical microscope:





Lower resolution: 200x Lower depth of focus: 15 µm





Higher resolution: 500,000x Higher depth of focus: 4 mm



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Image formation in a SEM





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ge formation in a SEM



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Image formation in a SEM



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Image formation in a SEM





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Image formation in a SEM





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Image formation in a SEM





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Image formation in a SEM





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Image formation in a SEM





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Image formation in a SEM





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Image formation in a SEM

> Electron beam – sample interaction:





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Image formation in a SEM

> Signals originated in the sample:



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Image formation in a SEM

> Signals originated in the sample:



Image formation in a SEM

> Secondary electrons:



Image formation in a SEM



Image formation in a SEM

> In-lens secondary electrons detector:





> Back-scattered electrons:



Image formation in a SEM

> Back-scattered electrons detector:





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Image formation in a SEM

> Secondary electrons image vs. Back-scattered electrons image:

Fe particles on carbon:



Secondary electrons Back-scattered electrons



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Image formation in a SEM

> Secondary electrons image vs. Back-scattered electrons image:

Pt particles on alumina:



Secondary electrons Back-scattered electrons







Image formation in a SEM

> Importance of the acceleration voltage: 2 keV



20 keV





>> At low voltage it is more sensitive to the surface because the penetration depth is lower.

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Image formation in a SEM

> Charging effects in a SEM:



Charging

(a) Fully Coating

(b) No Coating



Conducting coating

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Compositional analysis in a SEM







>> The energy of the X-rays generated is characteristic of each element, so one can performed a quantitative compositional analysis.



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Compositional analysis in a SEM

> X-ray microanalysis in a SEM (EDX):



>> Chemical mapping:













Concept:

Definition of submicrometric patterns by means of the electron beam scanning on a material (resist) sensitive to electronic irradiation





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Aspects of the SEM to consider for the application in EBL:

SEM emitter:

-The brightness of the electron emission is important, so, field-emission sources are better than thermionic sources.

- The stability is also important, so because of the current instability, cold FEG is not good choice for EBL, though it is the best for SEM imaging applications.



Emission	Therm	Field emission		
Emission	W	LaB ₆	FE	
Brightness (A/cm²/sr)	104 - 105	10 ⁵ – 10 ⁶	10 ⁷ – 10 ⁹	
Energy spread (eV)	I — 5	0.5 – 3.0	0.2 – 0.9	
Lifetime (h)	>20	>100	>300	
Vacuum (torr)	10 ⁻⁴ – 10 ⁻⁵	10 ⁻⁶ – 10 ⁻⁷	10 ⁻⁹ - 10 ⁻¹⁰	



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Aspects of the SEM to consider for the application in EBL:

Acceleration voltage and electron column quality:

- The acceleration voltage and the microscope resolution are relevant parameters.
- λ = 1.2 / (V_a)^{1/2}; for example λ = 0.008 nm at 25 kV.

- The acceleration voltage is important for the resolution because of the optical aberrations and the interaction of the electron beam with the resist and the sample.

Emission	Therm	Field emission	
Emission	W	₩ LaB ₆	
Source size	25 µm	10 μm	5 – 20 nm
Energy spread (eV)	I – 5	0.5 – 3.0	0.2 – 0.9

- The energy spread of the electron emission combined with the collimation, focusing and the column chromatic aberration will be important to determine the process maximum resolution.



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Aspects of the SEM to consider for the application in EBL:

Electron beam size on the resist:



• diffraction limit, $d_d = 0.6 \lambda/\alpha$

 λ = 1.2 / $\sqrt{V_e}$, electronic wave length






Aspects of the SEM to consider for the application in EBL:

Electron penetration in the sample: The acceleration voltage is important for the resolution and for the proximity effect.



Effect of beam energy for exposure of 100 nm of PMMA on bulk Si.

10keV







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Aspects of the SEM to consider for the application in EBL:

Proximity effect: Dense patterns worsen the resolution because of unintentional changes in the actual electro dose.





Real dose due to the proximity effect.



Target

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Resists for EBL:

- Most of resists are organic and can be positive or negative.
- The secondary electrons produced by the primary electron beam induce the break of the polymers (positive resist) or the cross-link (negative resist).

- **PMMA, poly(methyl methacrylate):** it is a positive electron-beam-sensitive resist widely used due to the good resolution achievable.



Generic reaction paths caused by EBL on PMMA.



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Resolution limit of EBL:

≈ 10 nm on insulating substrates:



Cross- section image.

The lithography is possible on the resist... and the transfer?

This is more complex due to the etching or the lift-off



S. Sangiao, J. M. De Teresa et al., *Nanotechnology* **27**, 505202 (2016). Introduction to Nanofabrication techniques





Fundamentals of FEBID:

FEBID: It is based on the electron-induced dissociation of a molecular precursor previously adsorbed on a substrate surface and constantly replenished by a gas-injection system (GIS).

It is a **direct-writing technique** in which the electron beam is provided by a SEM:





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3D capabilities of FEBID:

True 3D Nanoprinting!





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Available precursors for FEBID:

Elements that can be deposited by FEBID:

Main **drawback**: Purity of the deposits grown by FEBID.

Most of FEBID materials reveal metalmatrix composition (metallic nano-grains in carbon matrix).



Purest FEBID material: FEBID-Co grown by using

the $Co_2(CO)_8$ precursor gas.



M. Huth et al., Beilstein J. Nanotechnol. 3, 597 (2012). J. M. De Teresa et al., J. Phys. D: Appl. Phys. 49, 243003 (2016).

(c)



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FEBID parameters:

Main parameters that govern the writing process:

- Primary-beam energy.
- Beam current.
- **Dwell time**: time for which the electron beam is held constant on a particular point on the surface.
- Pitch: distance between neighboring dwell points.
- **Loops**: Number of loops for which the writing pattern is repeated.
- **Replenishment time**: Period for which the writing is paused between two successive loops.





M. Huth et al., Beilstein J. Nanotechnol. **3**, 597 (2012). Introduction to Nanofabrication techniques



Lateral resolution of FEBID:

FEBID deposits are broader than the electron beam profile because of the electron interaction volume:





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Applications: FEBID on insulating flexible substrates:

FEBID can be performed on insulating and FLEXIBLE polymer substrates.



The functionality of FEBID nanodeposits on flexible substrates is maintained over a huge range of bending angles! New applications, such as nano-optics, become possible!

P. Peinado, S. Sangiao and J. M. De Teresa, ACS Nano 6, 6139 (2015).





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Thank you for your attention!





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