Outline

- Introduction
- Laser durability at high energy
- Evaluation methods
- Subsurface damage
- Model formulation for laser damage
- Conclusions

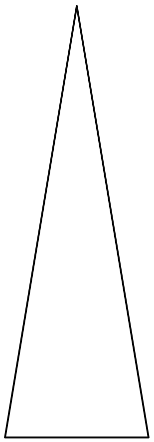
Shrink Roadmap of IC and Lithography Tool Makers

$$\text{Resolution} = k_1 \frac{\lambda}{n \sin \theta}$$

$$= k_1 \frac{\lambda}{NA}$$

CaF_2 application and material requirements for VUV Microlithography

CaF_2 areas of application



- ➢ Lenses for Projection Systems
- ➢ Lenses for Illumination Systems
- ➢ Rods for Alignment
- ➢ Beam Delivery Systems
- ➢ Excimer Optics for Laser Systems

The typical specified material requirements are:

- size (incl. tolerances)
    - diameter (up to 300 mm)
    - thickness (up to 80 mm)
- absolute refractive index
- dispersion
- change of refractive index from lot to lot
- homogeneity (dn < 1ppm)
- stress birefringence (< 1nm/cm)
- transmission (> 99,9%)
- radiation induced damage
- fluorescence
- stray light
- internal quality (real structure)

Key material parameters for lens blanks used in lithography tools

CaF_2 Material Parameters	Influence on Lithography Tool	Consequences for Material Supplier
Stress Birefringence	Image contrast	Profound understanding of physical properties is necessary in order to enhance growth process and subsequent treatment
Refractive Index Homogeneity	Image quality	
		Control contamination to ppb level, avoiding precipitations and inclusions

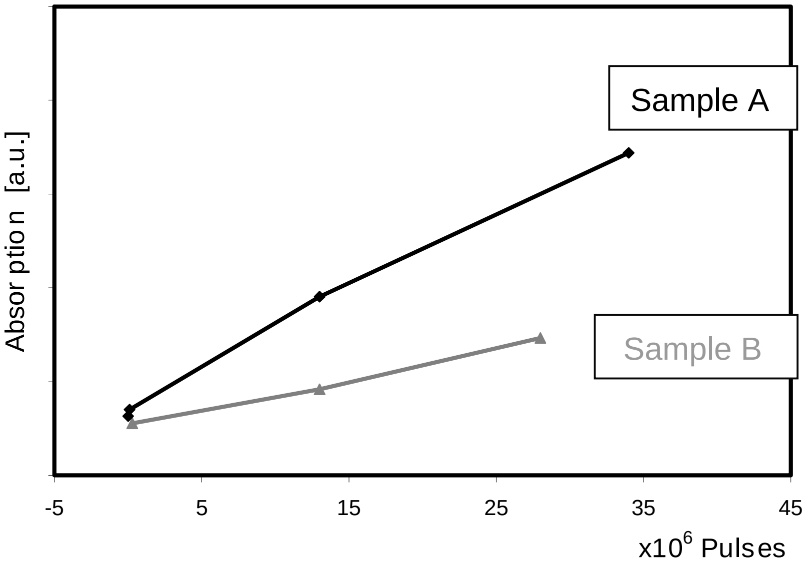
- High repetition rate laser light sources enabling high illumination power and wafer throughput are a fundamental prerequisite for high volume chip production.
- Higher Laser output power is necessary (present 20 W, expectation > 60 W)

Laser induced fluorescence (LIF)

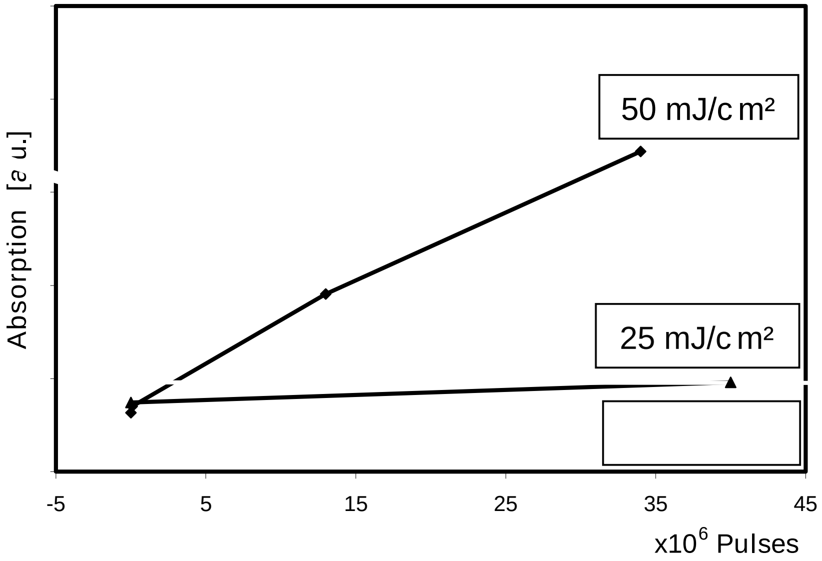
Visual observations

Durability of CaF_2 under ArF laser irradiation

- with 50 mJ/cm²



- with different energy



- What is the reason for the different degradation behavior ?
- Both sample have high transmission values @193nm in the range of about 99,8% !

- No or only very weak degradation up to 25 mJ/cm²
- Below 25mJ/cm² stable for >> 10^6 Pulses

Evaluation methods for Laser durability

1. Long time test regarding the field condition (several GPulses)
   → Very costly and time-consuming (several month)
2. Higher fluence and less pulse rate
   → Uncertainty of fluence dependence (~H^2, ~H^3 ?), strong exposure of equipment (lens, mirror etc)
3. Combination of different short time method e.g. :
   a. X-Ray – Damage
   b. Laser induced fluorescence (LIF)
   c. Initial absorption
   d. Transmission @157nm / @193nm
   e. ….
   → Any method doesn't clearly correlate with degradation behavior @193nm

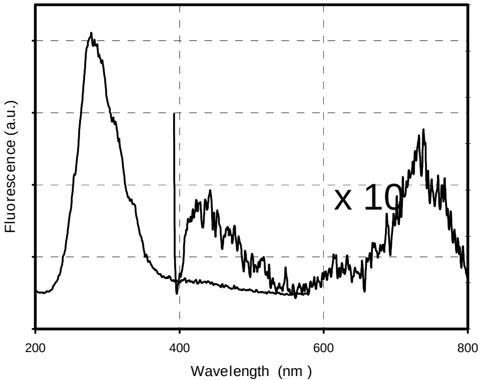
Correlation LIF – Transmission (non-irradiated)

Fluorescence @	Characteristic properties: (compared to intrinsic LIF only)	Influence on T_0 and Fluence
278nm Intrinsic (STE)	- Material independent LIF intensity - Very high values for T_0 - Different values for T_0: scattering? - Very low slope values $\lvert dT/dH \rvert$	Best available transmission properties
313 and 333nm	- Values for T_0 / slope $\lvert dT/dH \rvert$ virtually unchanged - No correlation between impurity concentration (I_{LIF}) and T_0 $\rightarrow$ scattering?	Very weak influence on T_0 and fluence dependent absorption
450nm	- Significant lower values for T0 - Weak correlation between impurity concentration (LIF) and T0 - Slope $\lvert dT/dH \rvert$ increases	Very strong influence on T_0 / strong influence on fluence dependent absorption
580nm	- Similar high values for T_0 - Slope $\lvert dT/dH \rvert$ increases by factor ~ 2	Strong influence on fluence dependent absorption / no influence on T_0
740nm	- Lower values for T_0 - No correlation between impurity concentration (ILIF) and T_0 $\rightarrow$ scattering? - Slope $\lvert dT/dH \rvert$ increases by factor ~3	Strong influence on fluence dependent absorption / weak influence on T_0

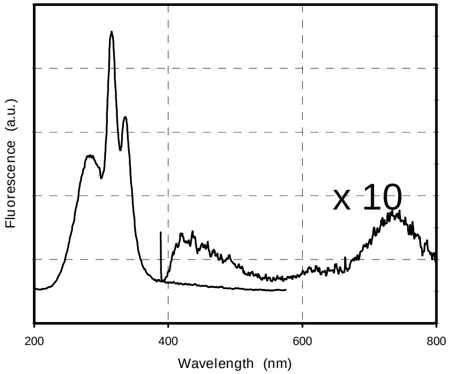
LIF spectra of CaF_2

- samples with weak (a, b) and good (c, d) laser durability

a.)

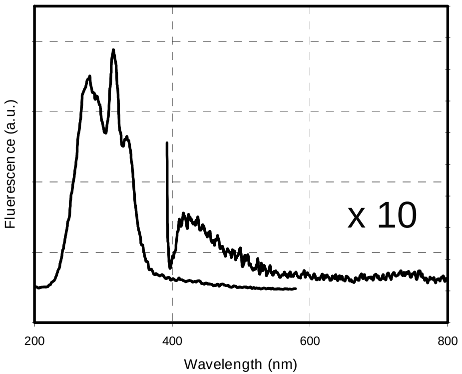


b.)

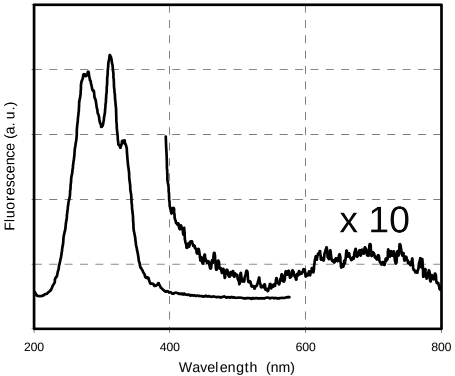


- Results confirm the correlation found for non-irradiated samples:
  - 740nm strongly determines fluence dependent absorption ,
  - great difference in 313/333nm – weak influence
- Different intensity of 740nm fluorescence but similar transmission loss !

c.)



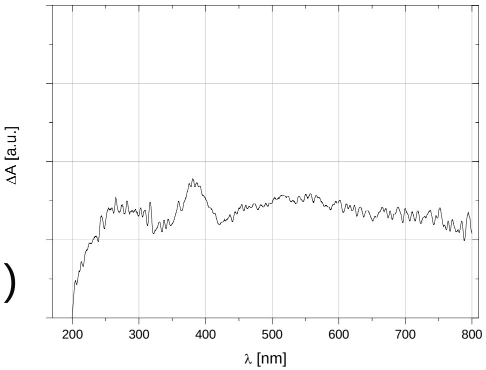
d.)



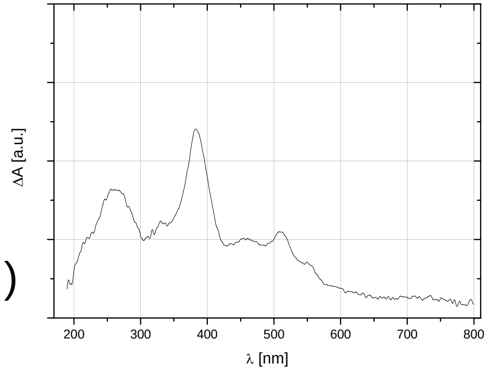
- Sample c.) confirms correlation for non-irradiated samples:
  - no observable fluorescence at 450nm, 580nm and 740nm
- Sample d.) is apparently in conflict : weak fluorescence at 740nm observed!

X-Ray damage spectra of CaF_2

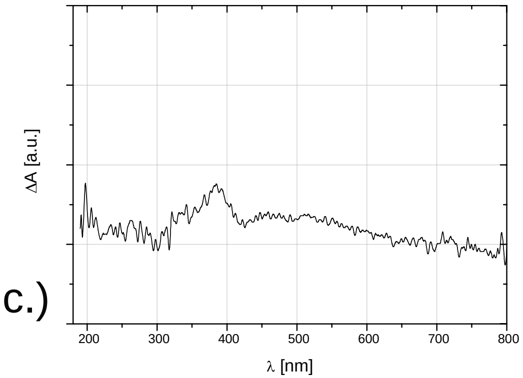
- with minor (a, b) and supirior (c, d) laser durability



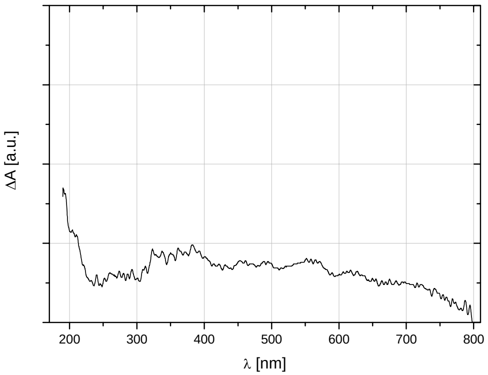
a.)



b.)



c.)



d.)

- The spectrum of the minor laser-durable crystal (a.) compares well to the spectrum of the stable crystal (c.)

Surface impact on laser degradation

1. Contact polishing (mechanical polish)
    a. Conventional polish (Diamond/SiC–slurry) - typical 0.5 - 0.6 nm RMS
    b. So-called super-polish (grain size < 0.1 µm) - roughness 0.2 - 0.3 nm RMS

    → Residual subsurface damage of ~200nm seems to be the lower limit, nearly independent on grain size (agree with Lit.), may related to the elastic/plastic properties of CaF2 (abrupt change at RT) – polycristalline /amorphous layers absorb

2. Contactless surface polish (additional finishing)
    a. Magnetorheological finishing (MHP) – 0.7 nm RMS (V.Libermann, 2002)
    b. Float-Polishing (ultra smooth) – 0.15 nm RMS (Y.Namba, 2004)
    c. Chemo-mechanical polish (CMP) – 0.1 - 0.2 nm RMS

    → Undisturbed atomic structure on surface,

(regardless RMS!)

AFM
10 x 10 µm²

MP
0.5 RMS

CMP
0.15 RMS

Surface roughness
(RMS)

0.7 nm

0.2 nm

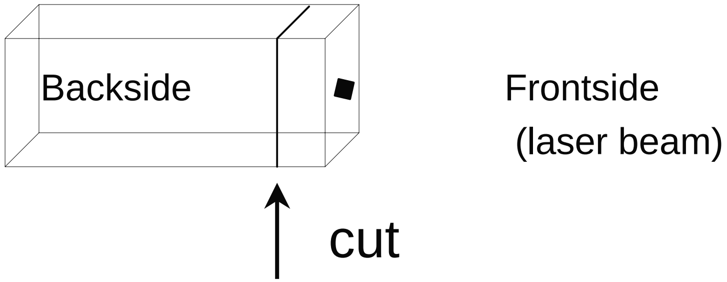
0.6 nm

V. Liberman et al 3rd Intern. Symp. On 157nm Lithography, Antwerp, 2002

Surface damage after laser irradiation

Measurement of surface reflectance with synchrotron radiation (PTB Berlin, Germany)

Wavelength = 90nm below the bandgap of CaF_2 (120nm)



Frontside: Transmission (@157nm) and reflection indicated the dimension of the laser beam spot (5mm – red arrow)

Backside: No defined reflectivity loss

AFM measurements show no increase of surface roughness in the damage area

➢ contamination (chemical change of the surface) and/or subsurface damage might occur

Model for Laser induced degradation

Model formulation and set-up:

1. Ideal, perfect periodic crystal lattice
    - two photon absorption
    - Frenkel pair (F^--H^+-pair), self trapped exciton (STE)
    - recombination of F^--H^+-pair (fluorescence at 278 nm, 1.1μs lifetime)
    - temperature dependent diffusivity of charge centers

2. Real lattice (with e.g. point defects, impurity ions, …)
    - (+) additional recombination paths for Frenkel pairs (lifetime reduction)
    - ( ) trapping mechanism
    - stable charge centers (impurity trapped F/H-center) at RT
    - agglomeration of charge centers (e.g. M-center)

Model for Laser induced degradation

Status of calculations:

For the ideal material rate equations are established
with well understood microscopic foundation

- Describes STE fluorescence and temperature dependence
- The Fluorine vacancies dominate, practical no F^- interstitials (H-Centers)

F-H-pair

e^- F_2^-

- Left: The STE (F-H-pair) can decompose into a F-center = trapped electron and a H (or V_k) center = trapped hole, two F-centers form a M-center
- Middle: Change of electronic density due to the formation of a F-Center.
- Right: Change of electronic density due to the formation of a H-center. The H-center is localized and accompanied by a huge lattice distortion

Atomic defect states in CaF_2 and trapping mechanism

1. Monovalent impurities (e.g. Li^+, Na^+, K^+)
   a. Replace Ca ion - positive charge stabilize a v_k-center (H-center)
   b. Interstitial lattice site – stabilize a F-center , occupied the octahedric gap in the fluorite structure
   c. Ca site and interstitial (pair of alkaline) - less probable (only for $2Li^+$)

2. Bivalent impurities (e.g. Mg^{2+}, Sr^{2+}, Ba^{2+}, O^{2-})
   a. Positive ions only on Ca site – stabilize charge center (H and F) but low trapping potential
   b. O^{2-} replace $2F^-$ (100 and 110-alignment) stabilize positive charge, v_k-(H)-center
3. Trivalent impurities (e.g. Al^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Y^{3+}, Ce^{3+}, Er^{3+})
   a. On Ca site – stabilize F-center like 1^+-interstitials

4. Multivalent impurities (e.g. $Fe^{2+/3+}$,$Mn^{2+/3+/4+}$, $Cr^{3+/6+}$, $RE^{2+/3+}$)
   a. Different coordination possible – trapping can occur but not necessary

The probability to be build into CaF_2 lattice is dependent on the ratio of ion radii and the lattice site/gap

Conclusions

- High purity perfect material with low defect structure increase the damage threshold
- The degradation based essentially on extrinsic defects (e.g. impurities, impurity associated F- and M-centers)
- Combination of independent short time method allow to replace the expensive long term evaluation of the laser durability with a high reliability. Single methods are not sensitive for all impurities/defects
- The subsurface damage and/or contaminations have a significant influence on the laser degradation and required an accurate surface preparation.
- A model for ideal crystal is established and describes both the intrinsic defect structure and the different defect states of impurities.

Outlook

- CaF_2 with high radiation hardness for higher laser energy is available for supporting both dry and wet ArF-Lithography
- The results give clear directions to well-defined removal of specific impurities (within raw materials and process) and support further improvement of the laser durability
- A refined model for ideal crystal will implement extrinsic defects in the band structure of CaF_2