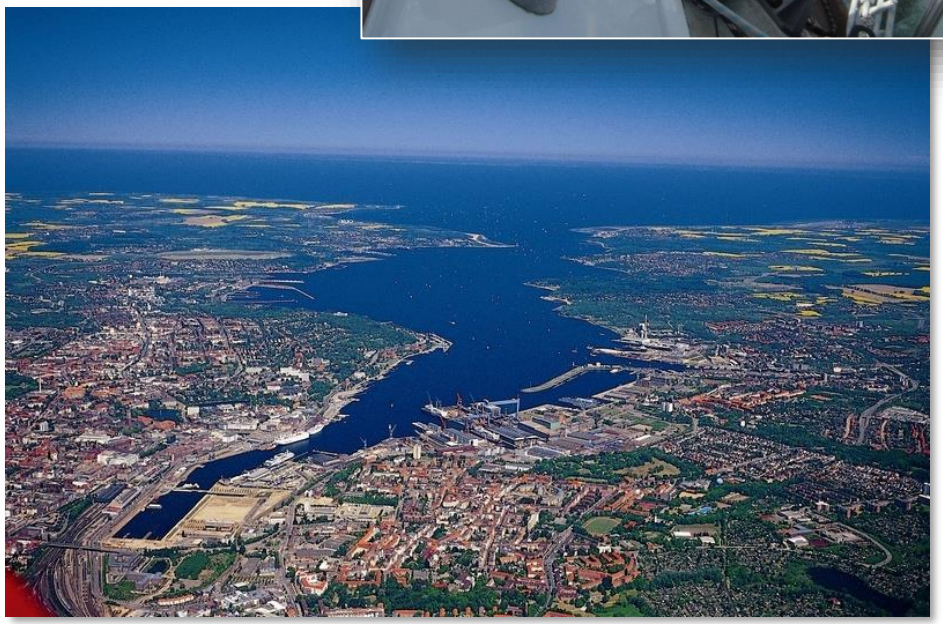
# Plasma Cleaning of Daguerreotypes

***Holger Kersten,*** *L. Hansen, L. Marxen, K. Neumann, T. Trottenberg, B. Renard**

*PlasmaTechnology / IEAP / University of Kiel, Germany, *FotoRenard, Strande, Germany*


**XXIX. Workshop OTPIP**
Mühlleithen 03/13/2024

# Kiel → Mühlleithen

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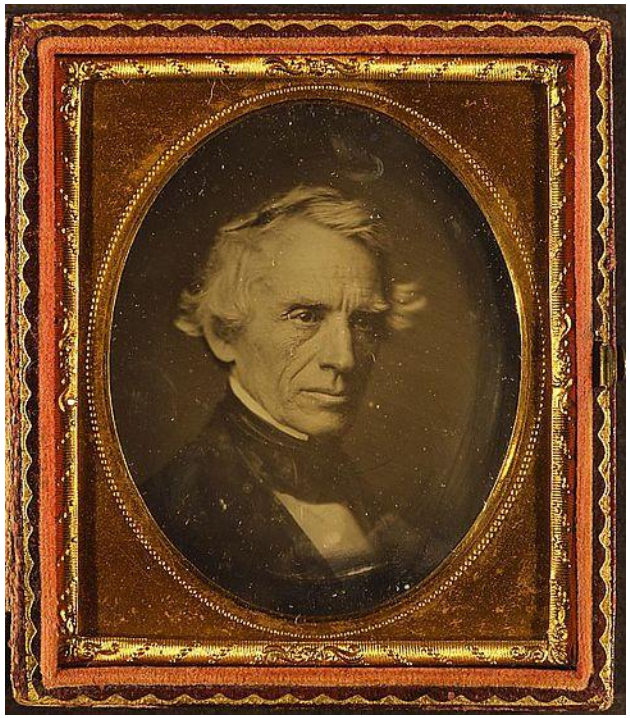
# introduction

# introduction

## daguerreotypes

- **daguerreotypes** represent the first practical form of photographs (~ 1840 … 1860)
- the image is formed by **light scattering at distributed (small) silver amalgam particles (microcrystals)** of varying size and density on a silver (or silver-coated copper) sheet

Daguerreotype (~1844) of ***Louis Daguerre*** (1787-1851)
L. Daguerre was one of the pioneers of photography and inventer of daguerreotypes



Daguerreotype (~1845) of ***Samuel Morse*** (1791-1872)
S. Morse was the inventor of telegraphy and introduced also daguerreotypes in the USA

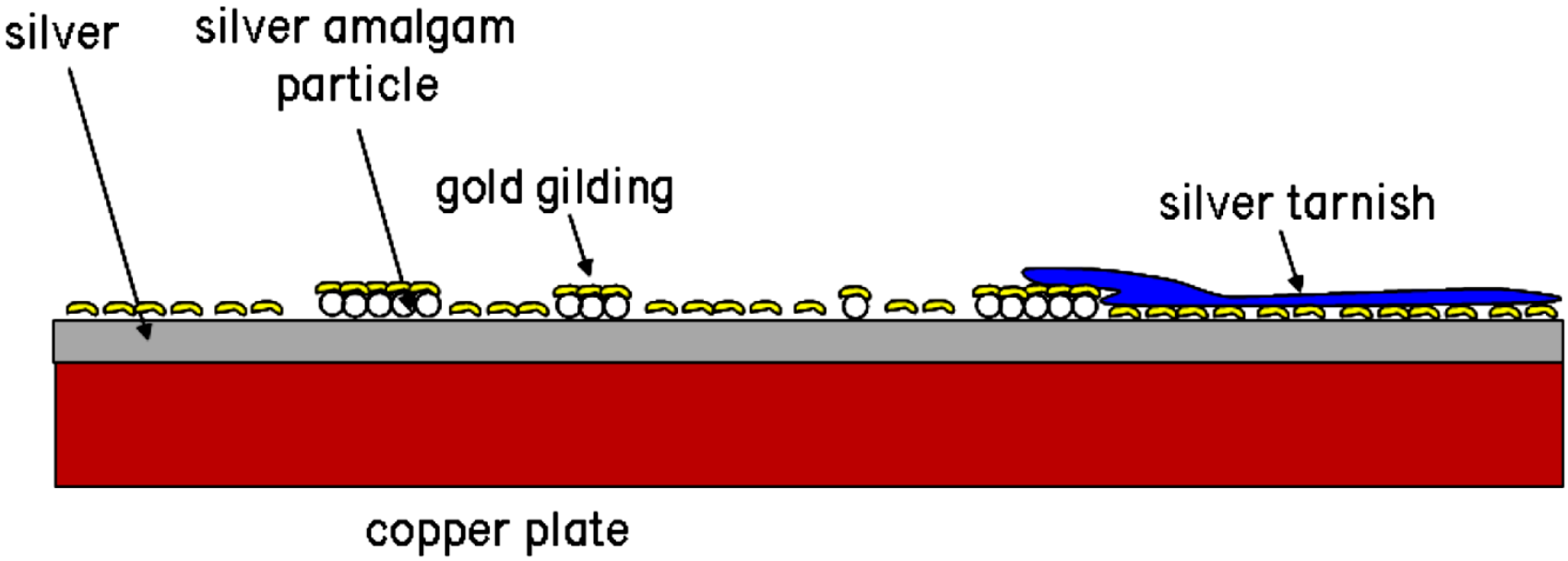
# introduction

## corrosion of daguerreotypes

# introduction

## corrosion of daguerreotypes

- through decades, 19th century daguerreotypes have generally suffered several **corrosion phenomena**, which remarkably reduced their historic and artistic value
- daguerreotype surfaces are typically covered by an **irregular tarnish layer** of varying composition
- mainly, exposure to atmospheric moisture and touching causes the formation of tarnish films by **silver compounds** (sulfides, oxides …)




*Boselli, M., Chiavari, C., Colombo, V., et.al., ICOPS-2013, San Francisco, 2013.*
*Wei, W., Gerritsen, I., von Waldthausen, C.,*
*Topics in Photographic Preservation, **14**(2011), 24-40.*

# introduction



- in a **corrosion process** (e.g. rusting of iron), metal (e.g. iron) atoms go into **solution**

$$M \longrightarrow M^{n+} + ne_0^-$$

- by this solution (so-called **anodic reaction**) electrons are released

- somewhere else on the surface, the electrons can recombine with the ions of liquid surroundings (e.g. moisture) such as *H+*, or attached to radicals to form negative ions such as *OH-* (so-called **cathodic reaction**)

$$2H^+ + 2e_0^- \longrightarrow H_2 \qquad O_2 + H_2O + 4e_0^- \longrightarrow 4OH^-$$

- the ions can recombine to **new compounds** (e.g. iron oxide) which form a **corrosion layer**

- these reactions can occur in various combinations

- quite similar, also sulfides, hydroxides, chlorides etc. are formed (e.g. $Ag_2S$)

# introduction

## corrosion of daguerreotypes

- quite similar, also sulfides, hydroxides, chlorides etc. are formed (e.g. $Ag_2S$)

- **tarnishing** is mainly produced by hydrogen sulfide ($H_2S$) which is present in air in very small amounts
- given access to a clean silver surface, this amount od hydrogen sulfide will cause a visible tarnish layer of **silver sulfide** ($Ag_2S$) in a few months

$$2Ag + H_2S \rightleftharpoons Ag_2S + 2H^+ + 2e$$

$$\frac{1}{2}O_2 + H_2S + 2Ag \longrightarrow Ag_2S + H_2O$$

- initially, the layer of silver sulfide is very thin causing **interference colours**
- but when it becomes thicker, the tarnish appears **brownish or black**
- if daguerreotypes are in frames and covered by glass, the hydrogen sulfide firstly get access to the silver surface at the outer edges due to moisture and enrichment

# introduction

## cleaning methods

- photo-conservation requires non-invasive cleaning methods for **controlled removal of corrosion products** without damaging the fragile image structure
- different approaches have been applied from first cleaning and restoration attempts:

- **chemical solvents** (cyanides, thioureas) caused fading of images and permanent spotting due to silver loss

  *Swan, A., Image, **21**(1978), 24-31.*
  *Barger, M.S., Krishnaswamy, S.V., Messier, R., JAIC, **22**(1982), 13-24.*

- **low-pressure non-thermal plasma cleaning** (~1980) for removal of tarnish causing a visible improvement in the appearance of cleaned daguerreotype surfaces

  *Barger, M.S., Giri, A.P., White, W.B., Edmondson, T.M., Studies in Conservation, **31**(1986), 15-28.*
  *Daniels, V., Studies in Conservation, **26**(1981), 45-49.*

- **electrochemical cleaning** with immersion in alkaline solutions

  *Barger, M.S., Giri, A.P., White, W.B., Edmondson, T.M., Studies in Conservation, **31**(1986), 15-28.*
  *Wei, W., Gerritsen, I., von Waldthausen, C., Topics in Photographic Preservation, **14**(2011), 24-40.*

- **thermal ablation by laser cleaning** (~2000) for selective treatment of specific areas

  *Turovets, I., Maggen, M., Lewis, A., Studies in Conservation, **43**(1998), 89-100.*
  *Golovlev, V.V., Gresalfi, M.J., Miller, J.C., Anglos, K, et.al., J. Cultural Heritage, **4**(2003), 134-139.*

- **atmospheric-pressure non-thermal plasma cleaning** (~2010) to avoid vacuum systems

  *Boselli, M., Chiavari, C., Colombo, V., et.al., ICOPS-2013, San Francisco, 2013.*
  *Grieten, E., Schalm, O., Tack, P., Bauters, S., Storme, P., et.al., J. Cultural Heritage, **28**(2017), 56-64.*

# conservation of daguerreotypes

# conservation of daguerreotypes

## electrochemical cleaning

- one can „turn arround“ the corrosion and put electrons back into the metal (**electrolysis**)
- by doing this, one can break up the corrosion products (e.g. rust) into the metal (iron) and oxygen – this process is called **reduction**

- this reduction process can also be used for the electrochemical cleaning of daguerreotypes as well as other silver objects

- the silver tarnish (mainly silver sulfide) is reduced

$$Ag_2S \longrightarrow 2Ag^+ + S^{2-}$$

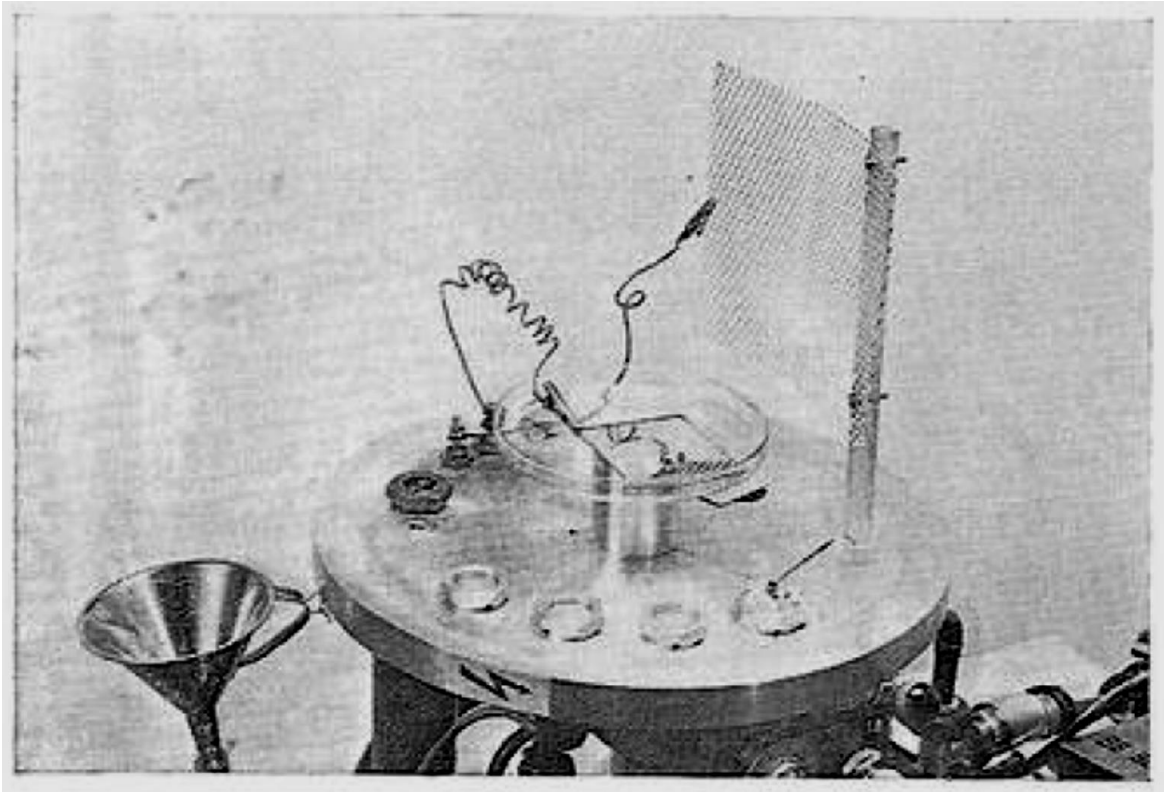
- the silver ions recombine with electrons to form silver again, while the sulfur ions recombine with *H+* ions to form (volatile) hydrogen sulfide

$$Ag^+ + e_0^- \longrightarrow Ag \qquad 2H^+ + S^{2-} \longrightarrow H_2S$$

# conservation of daguerreotypes

## plasma cleaning

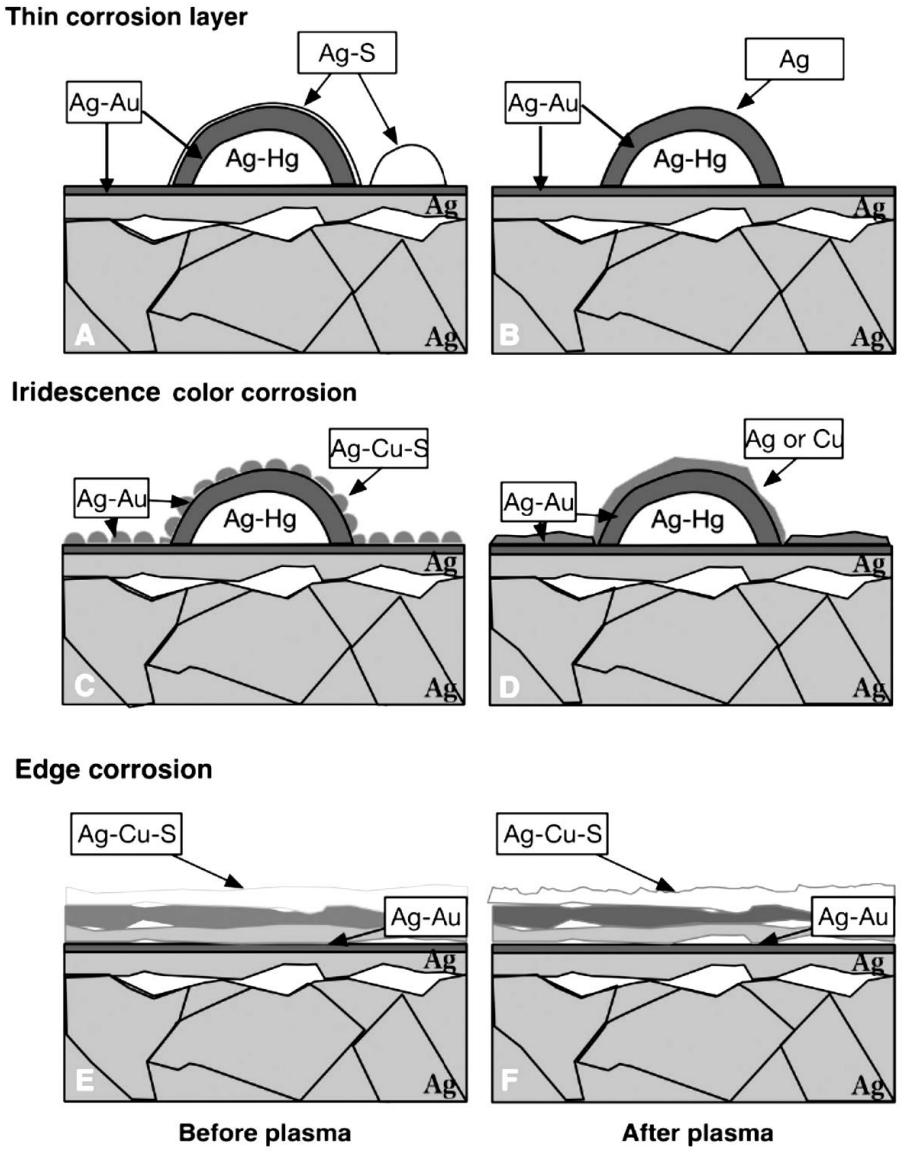
- instead in **wet electrolytic solution**, the charge carriers (ions and electrons) as well as reactive radicals (*H*) can be produced by a **dry glow discharge**
- effects of direct ion impact (**physical sputtering**) and afterglow (**chemical reactions**)
- the daguerreotype can be used as **electrode** of the discharge or as **floating substrate**



*Daniels, V.,*
*Studies in Conservation, **26**(1981), 45-49.*

# conservation of daguerreotypes

## plasma cleaning




*Grieten, E., Schalm, O., Tack, P., Bauters, S., Storme, P., et.al., J. Cultural Heritage,* ***28****(2017), 56-64.*

**reduction of thin corrosion layer** ($Ag_2S$) to metallic film ($Ag$)

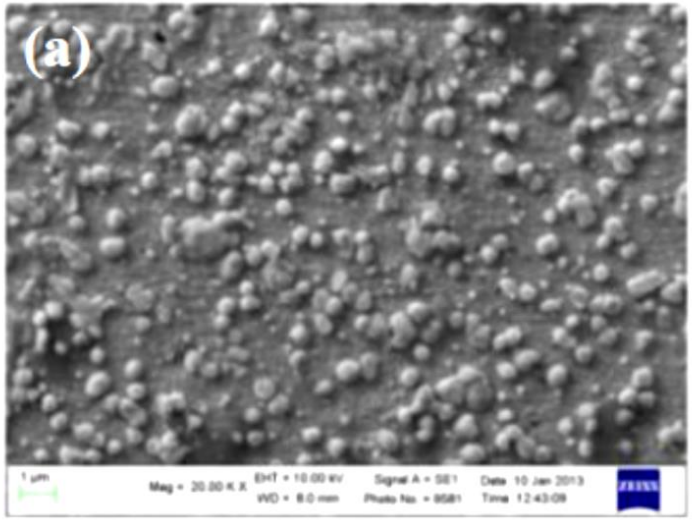
**removal of nanoparticles** of ($Ag_2S$) to metallic film ($Ag$)

afterglow plasma is not able to reduce thick corrosion layer composed of **ternary compounds**

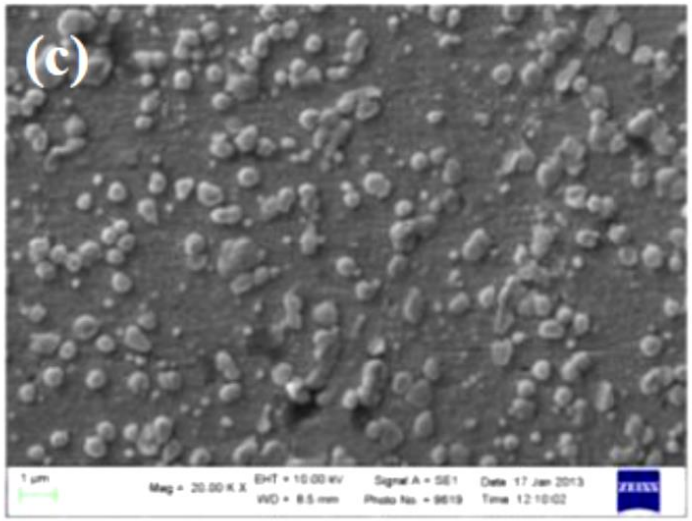
# conservation of daguerreotypes

## plasma cleaning

before




after




plasma treatment do not alter the **surface morphology**, with particular regard to features characterizing the grey levels of the images (e.g. shape or number of particles of amalgam (Ag-Hg))

the morphological features need to be preserved in order to maintain the contrast of the image

*Boselli, M., Chiavari, C., Colombo, V., et.al., ICOPS-2013, San Francisco, 2013.*

# plasma cleaning

# plasma cleaning

## removal of hydrocarbon (oil, grease) contaminants by glow discharge plasma

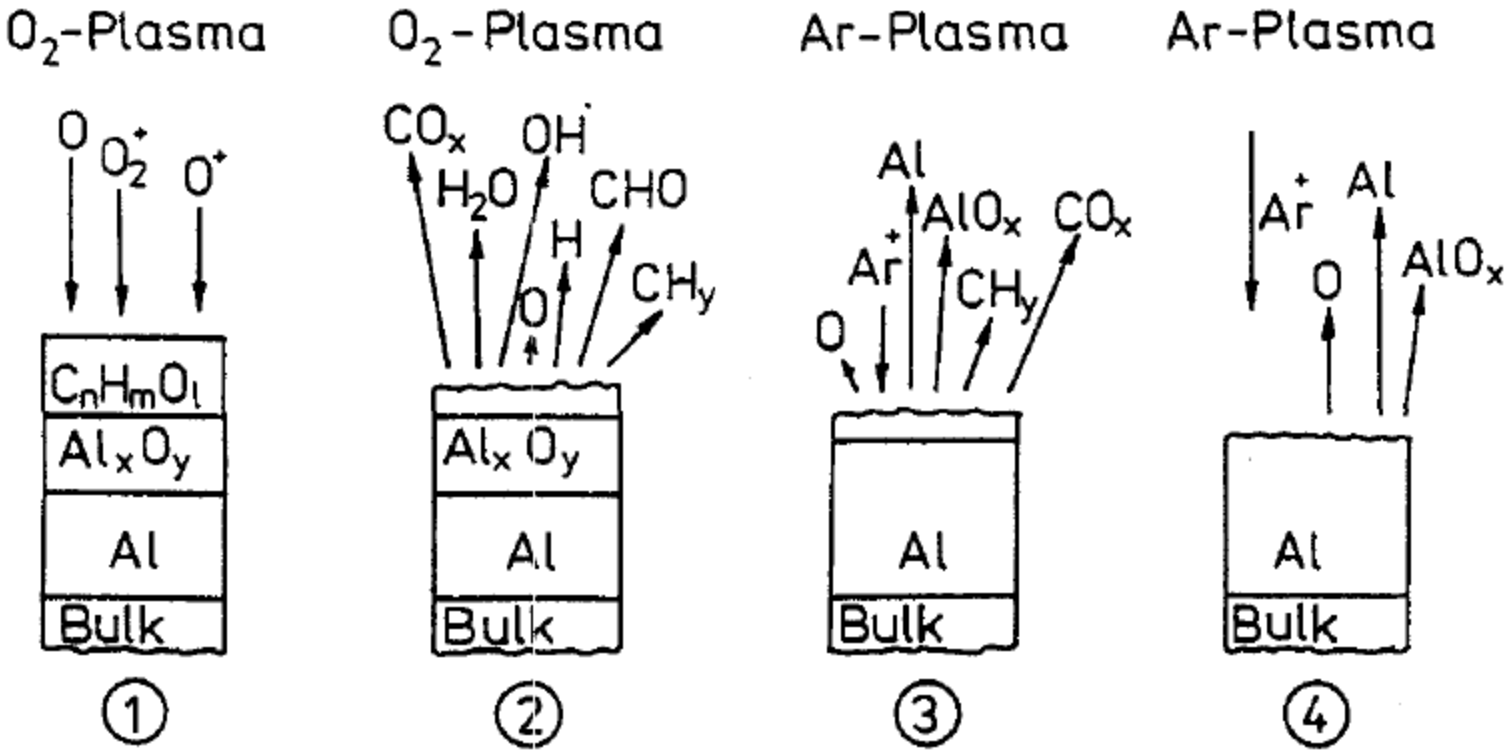
*Kersten, H., Behnke, J.F., Eggs, C., Contrib.Plasma Phys.* ***34****(1994), 563.*

*Steffen, H., Schwarz, J., Kersten, H., Behnke, J.F., Eggs, C., Thin Solid Films* ***238****(1996), 158.*

# plasma cleaning

## basic mechanisms

1. chemical surface film reactions (SFR) of the organic layers with oxygen atoms which are produced in the collision dominated cathode fall and in the negative glow by dissociation of $O_2$-molecules,
2. chemical sputtering (CSP) with high energetic $O_2^+$- and $O^+$-species colliding with the cathode,
3. physical sputtering (PSP) of the cathode material ($CH_xO_y$-layer, native oxide and metal) with $Ar^+$-ions.



# plasma cleaning

## basic mechanisms

The following impact processes take place in the cathode fall and in the glow:

$$O_2 + e_f \rightarrow O_2^+ + 2e_{f'}, \quad (1)$$

$$O_2 + e_f \rightarrow O^+ + O + 2e_{f'}, \quad (2)$$

$$O_2 + e_f \rightarrow O + O + e_{f'}. \quad (3)$$

decay into more stable negative atom ions and oxygen atoms:

$$O_2 + e_l \rightarrow O_2^-, \quad (4)$$

$$O_2^- \rightarrow O^- + O, \quad (5)$$

$$O_2^- \rightarrow O + O + e_l. \quad (6)$$

The prefered building processes of negative ions also contribute to the formation of reactive oxygen atoms:

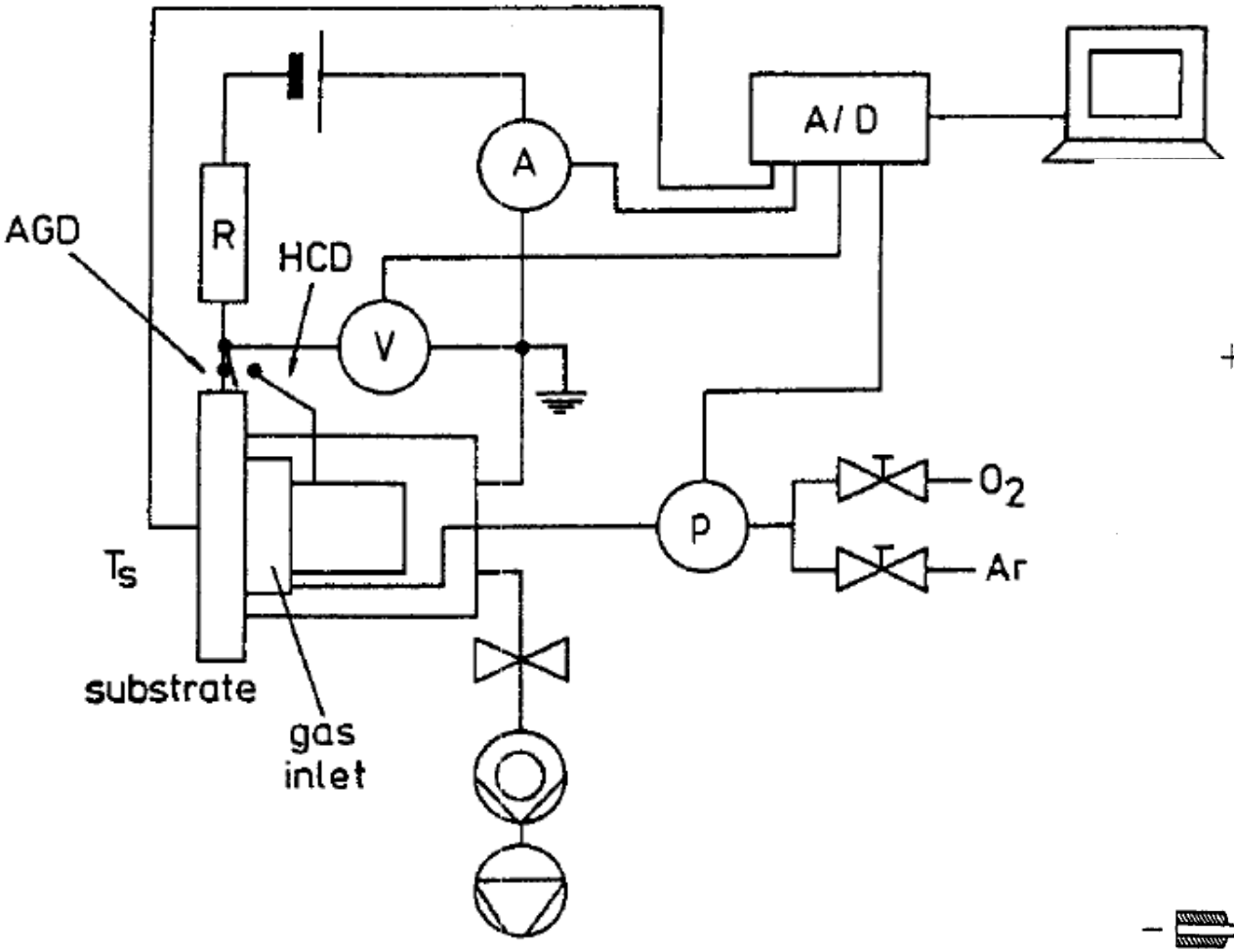
$$O^- + O_2 \rightarrow O + O_2^-, \quad (7)$$

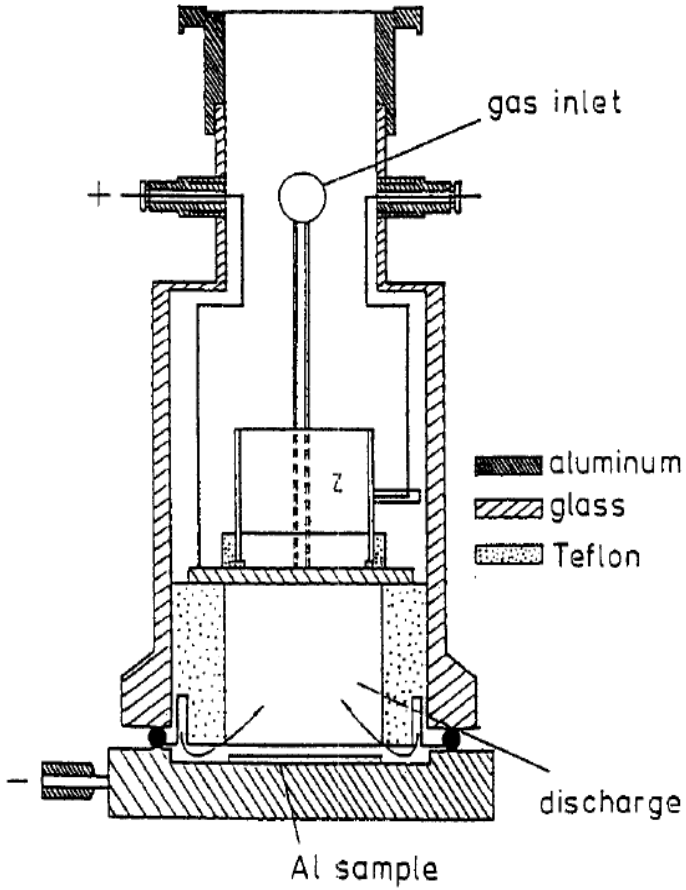
$$O^- + O_2 \rightarrow O^+ + O_2 + 2e_l. \quad (8)$$

$$j_O = \frac{1}{4} n_O \sqrt{\frac{8kT}{\pi m_O}} \approx 9.1 \cdot 10^2 n_O \sqrt{T} \quad [\mathrm{cm^{-2}\,s^{-1}}]$$

# plasma cleaning

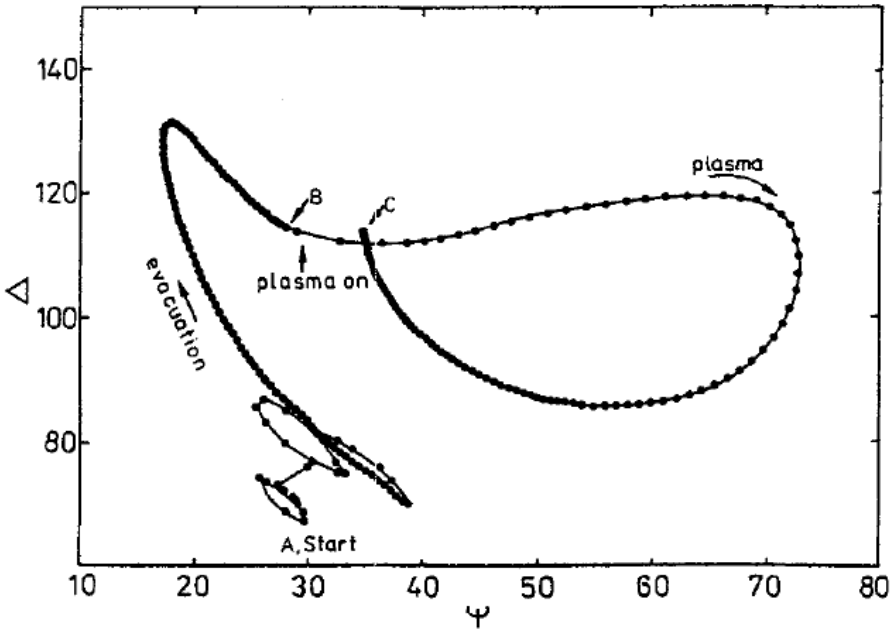
## experiment: HCGD, AGD

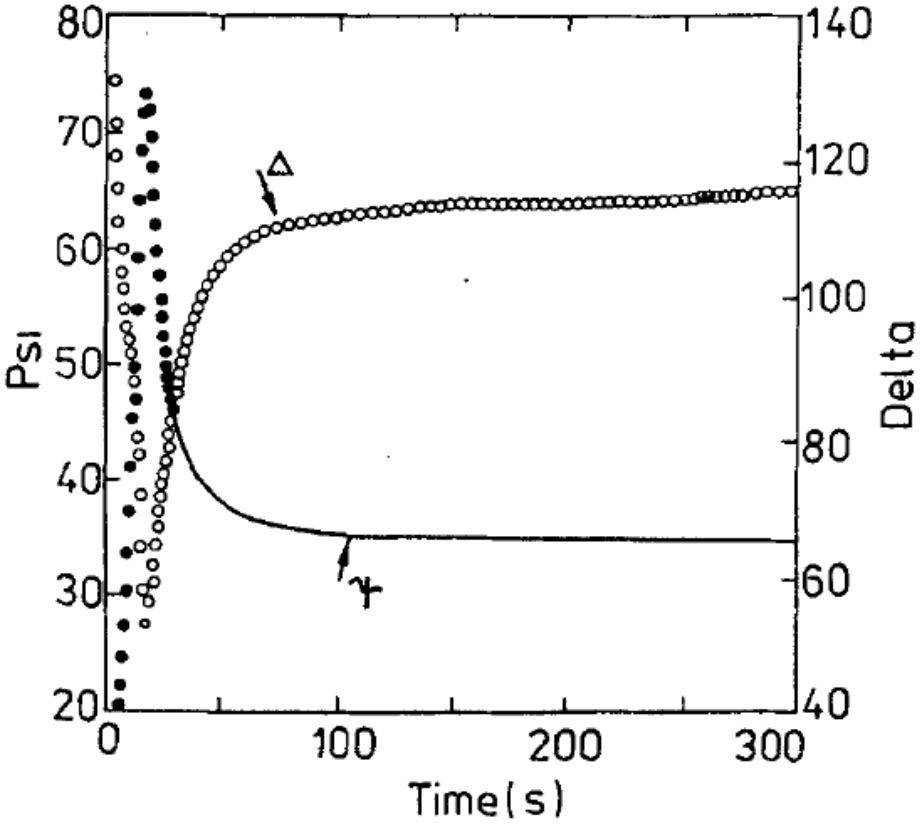


# plasma cleaning

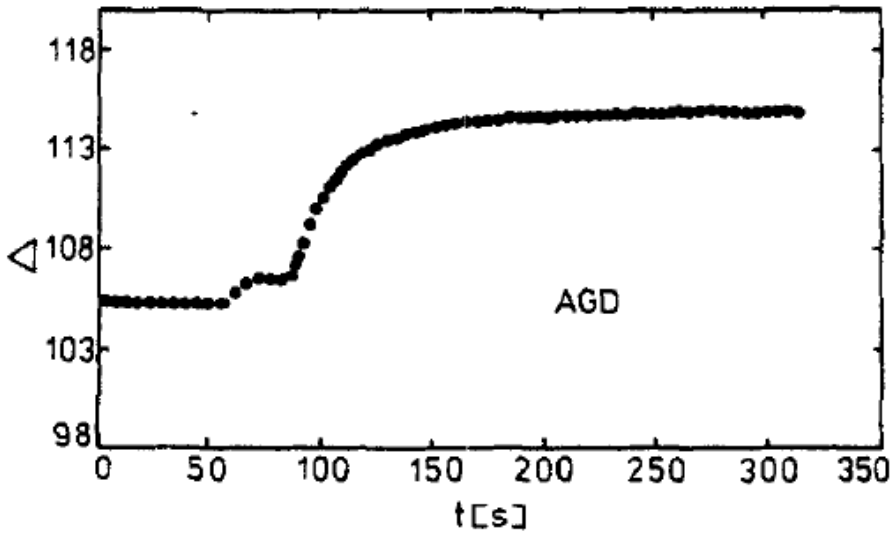
## ellipsometry

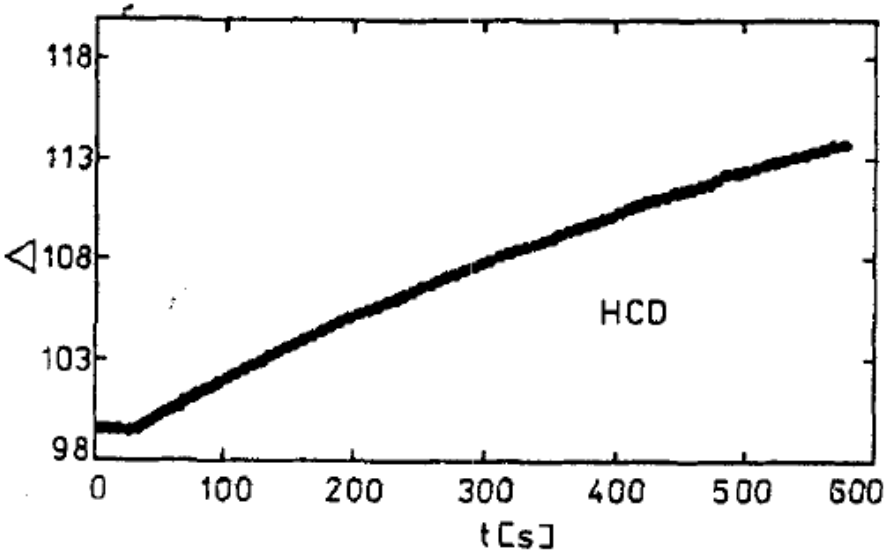


# plasma cleaning

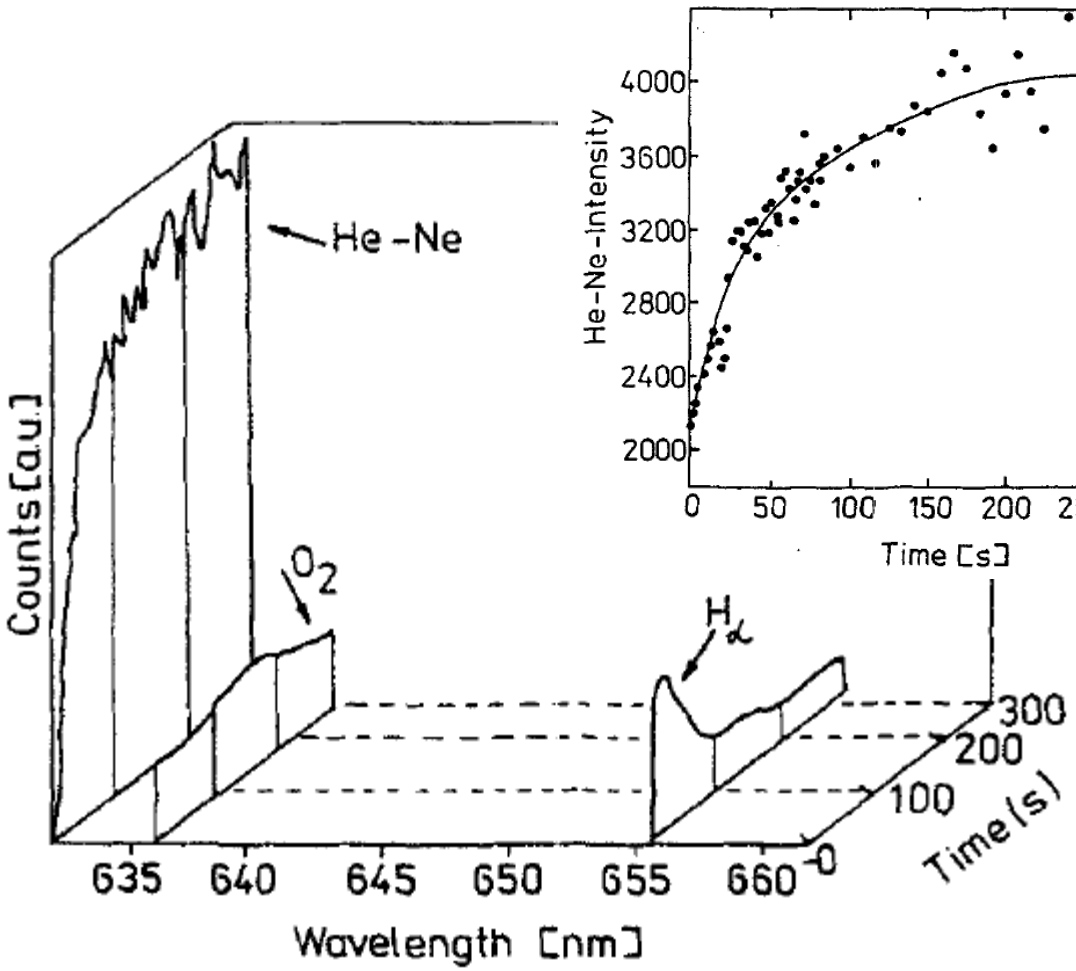
ellipsometry



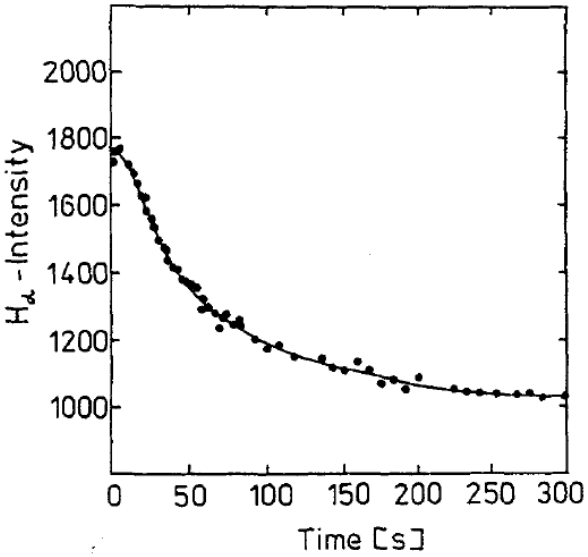
# plasma cleaning

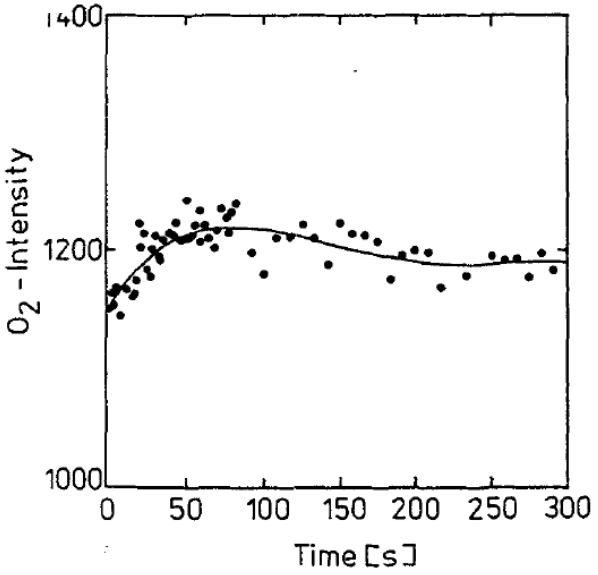
OES







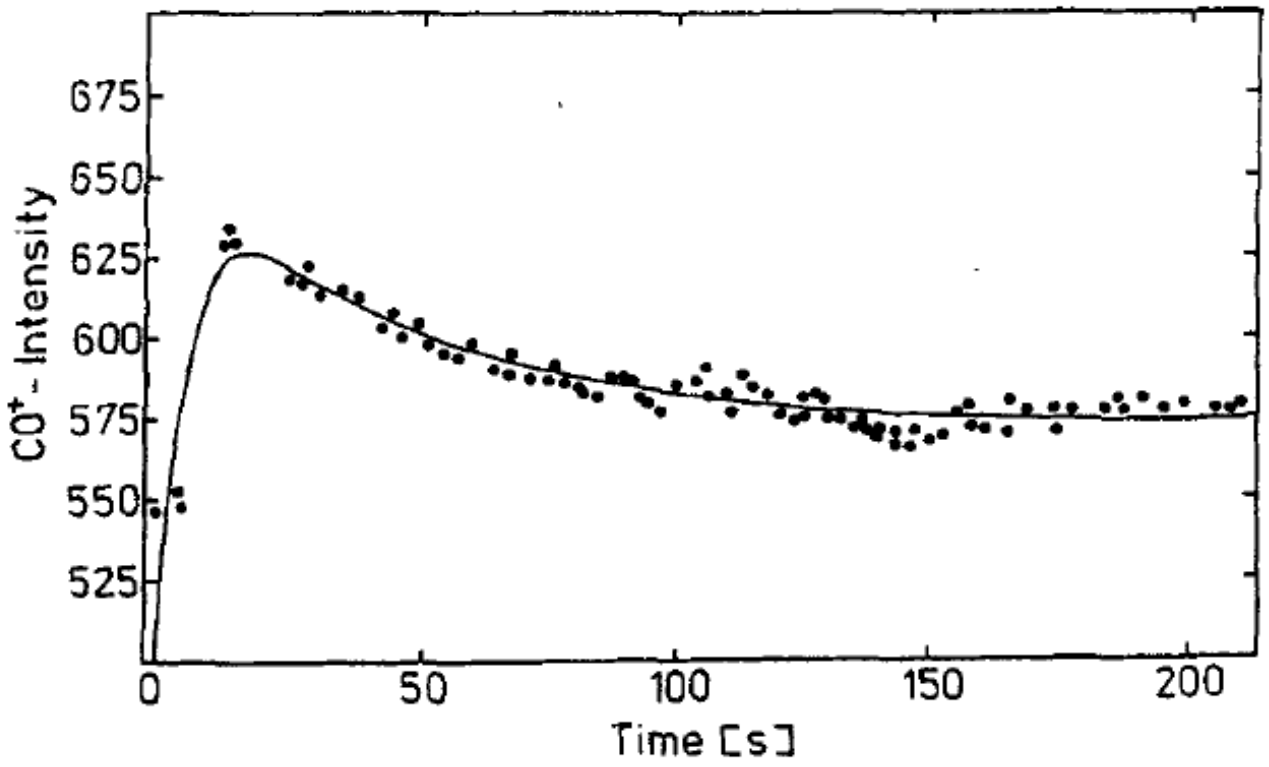



*Kersten, H., Behnke, J.F., Eggs, C.,*
*Contrib. Plasma Phys.* ***34****(1994), 563-574.*

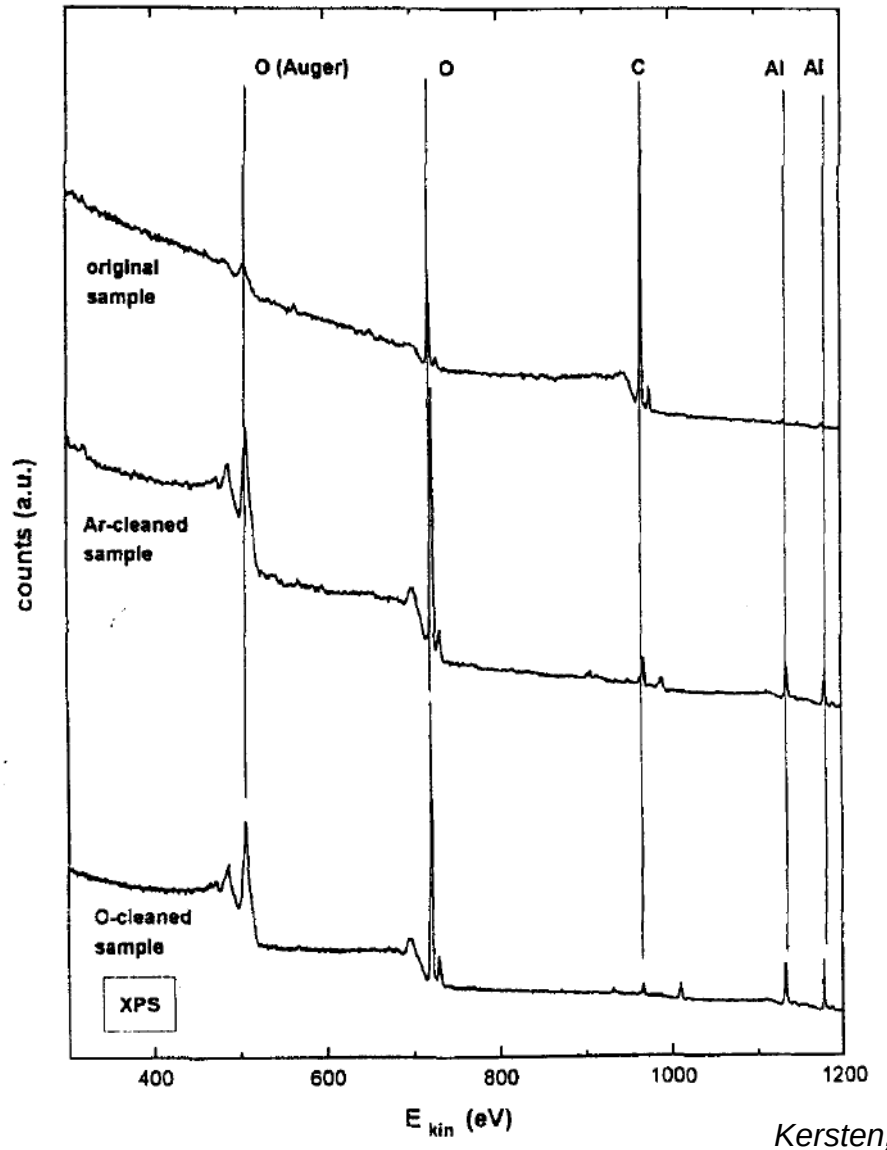
# plasma cleaning

OES



# plasma cleaning

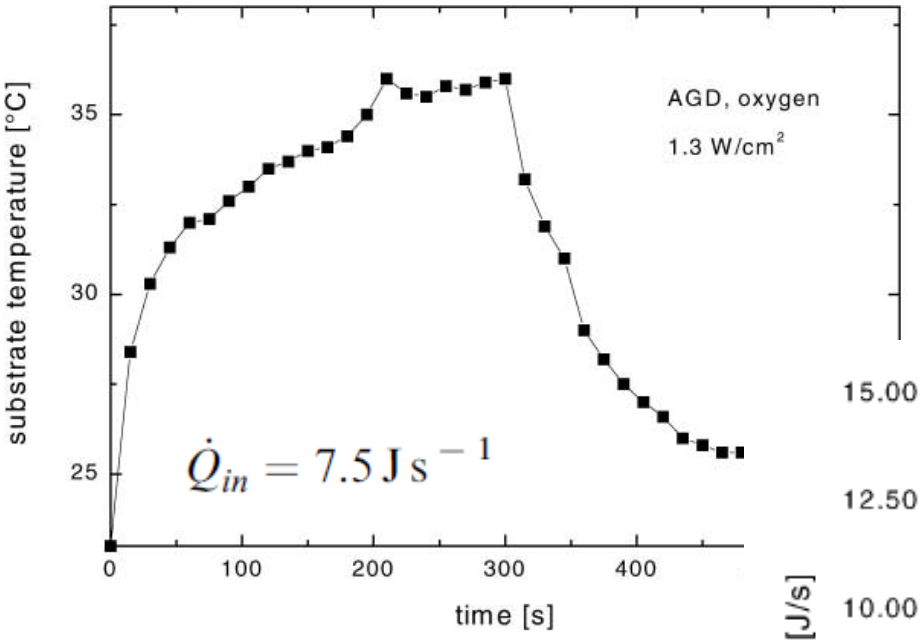
XPS




*Kersten, H., Behnke, J.F., Eggs, C., Contrib. Plasma Phys.* ***34****(1994), 563.*

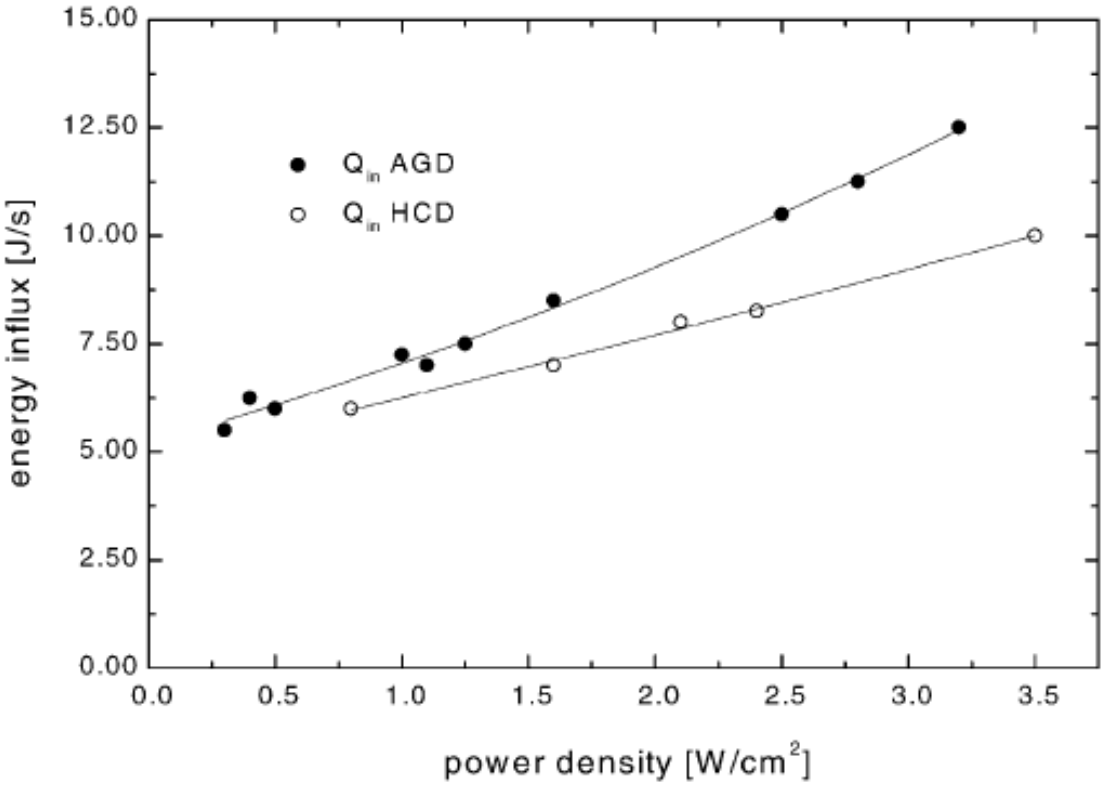
# plasma cleaning

## energy influx




$$T_S(t) = T_H + \frac{\dot{Q}_{in} d}{\lambda A}\left(1 - \exp\left(-\frac{\lambda}{d^2 \varrho c_P}\right)\right)$$

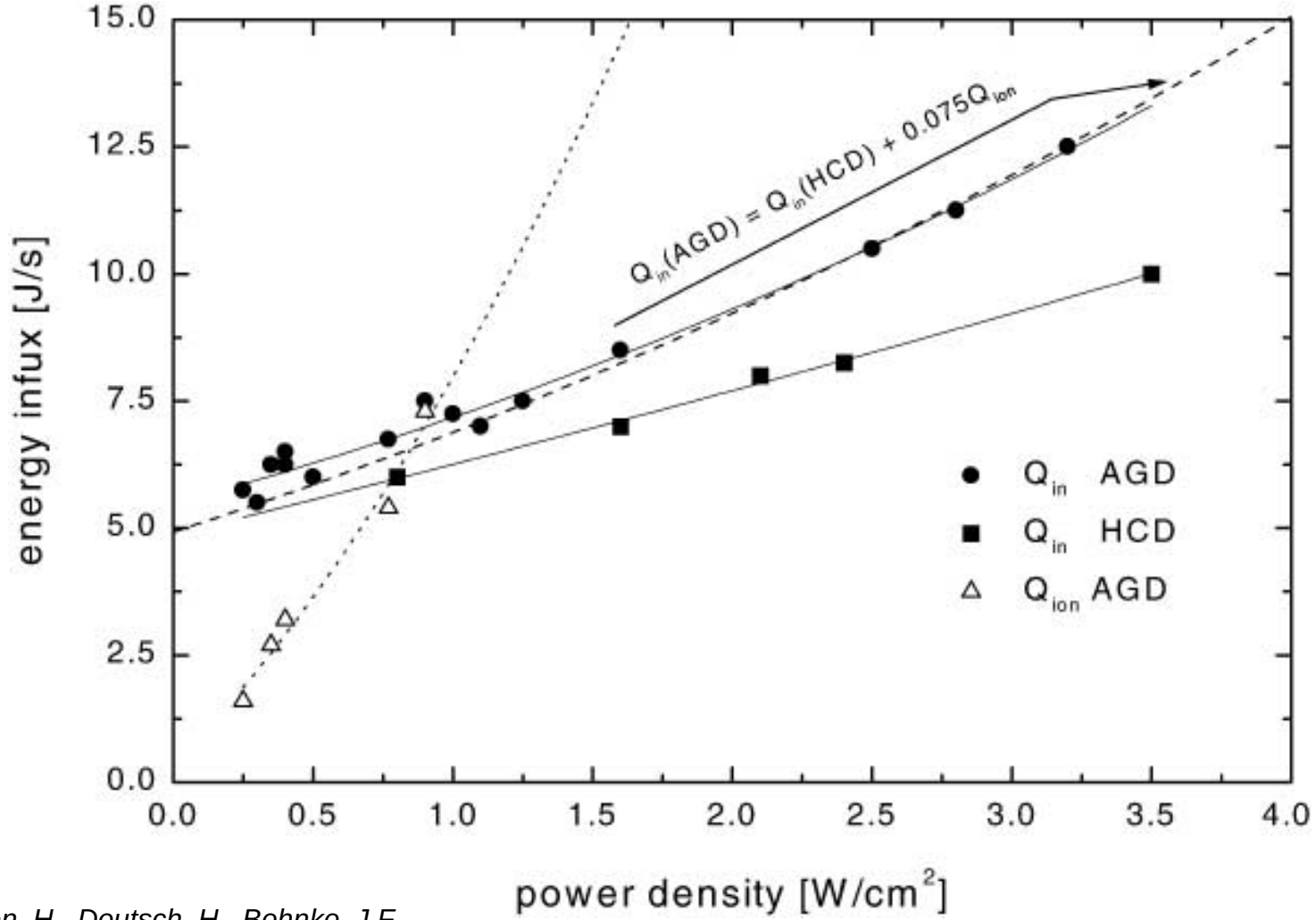
$$\left(\frac{dT_S}{dt}\right)_{t=0} = \frac{\dot{Q}_{in}}{d_S A_S \varrho c_S}$$




*Kersten, H., Deutsch, H., Behnke, J.F., Vacuum **48**(1997), 123-128.*

# plasma cleaning

## total energy influx

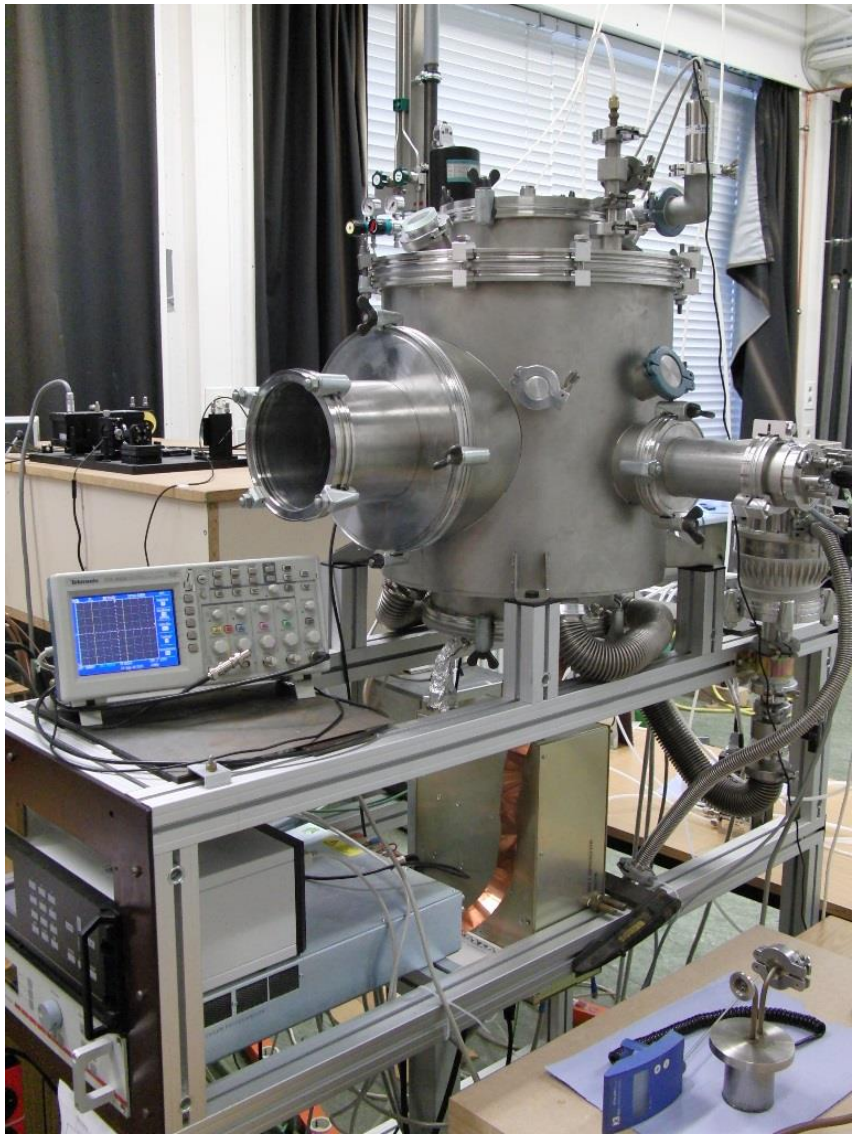



*Kersten, H., Deutsch, H., Behnke, J.F., Vacuum* ***48****(1997), 123-128*.

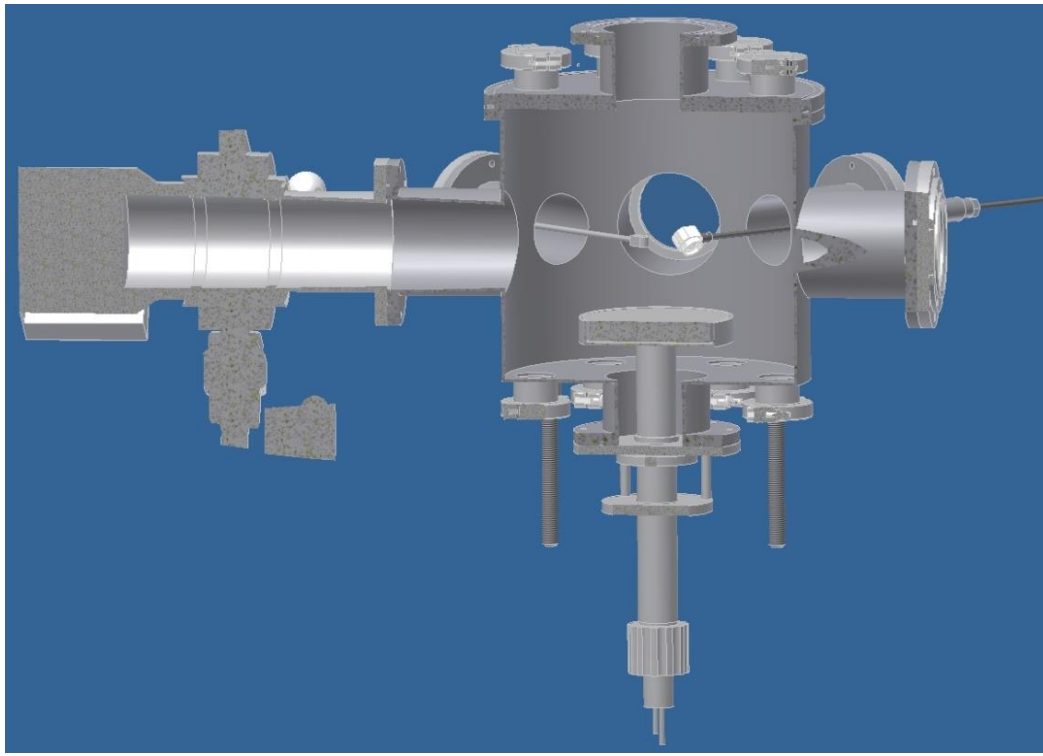
# plasma cleaning of daguerreotypes

# plasma cleaning of daguerreotypes

rf plasma



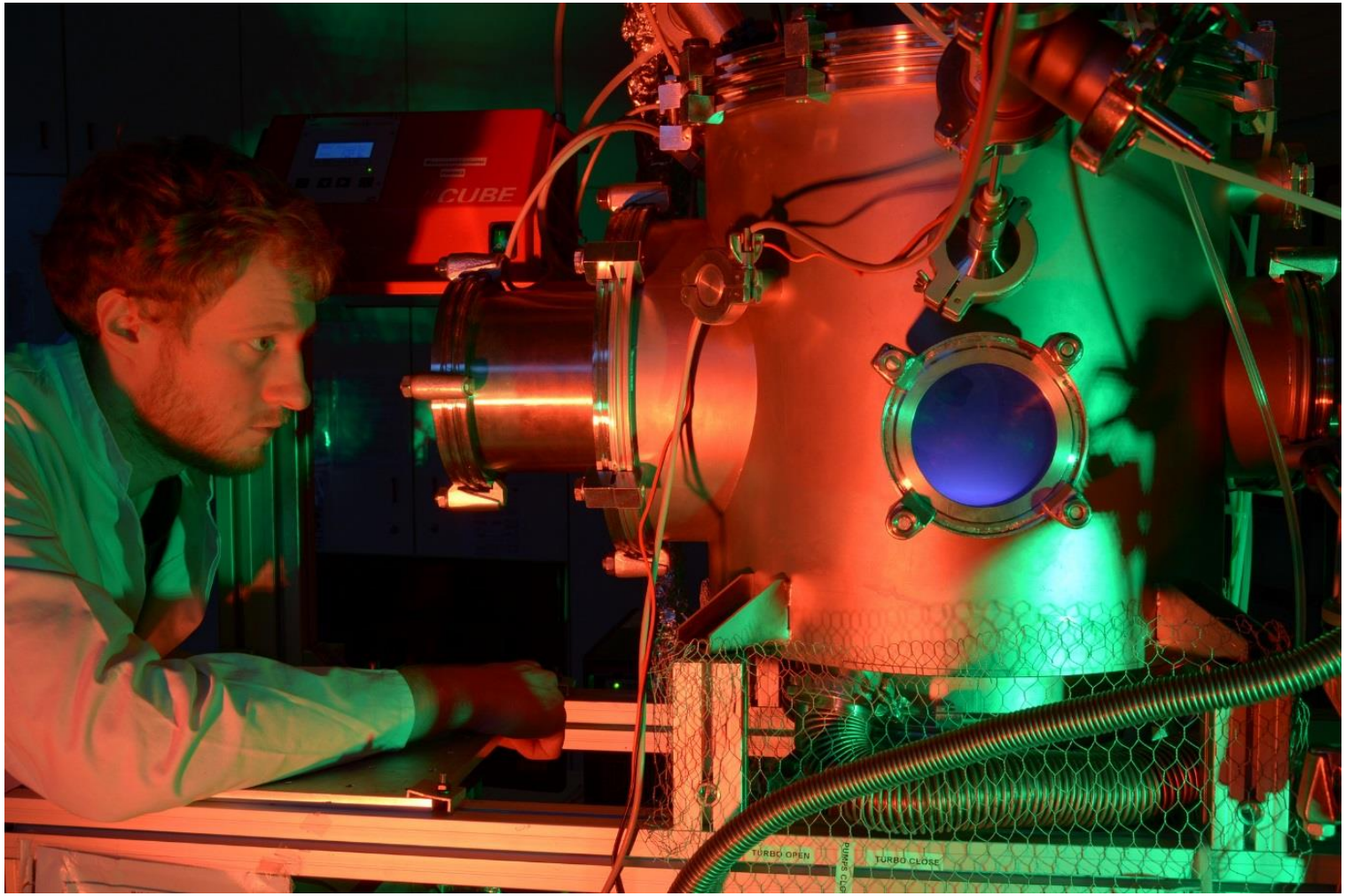
**ATILA**



*M.Wolter, M.Stahl, H.Kersten, Vacuum **83** (2009) 768–772.*

# plasma cleaning of daguerreotypes

rf plasma

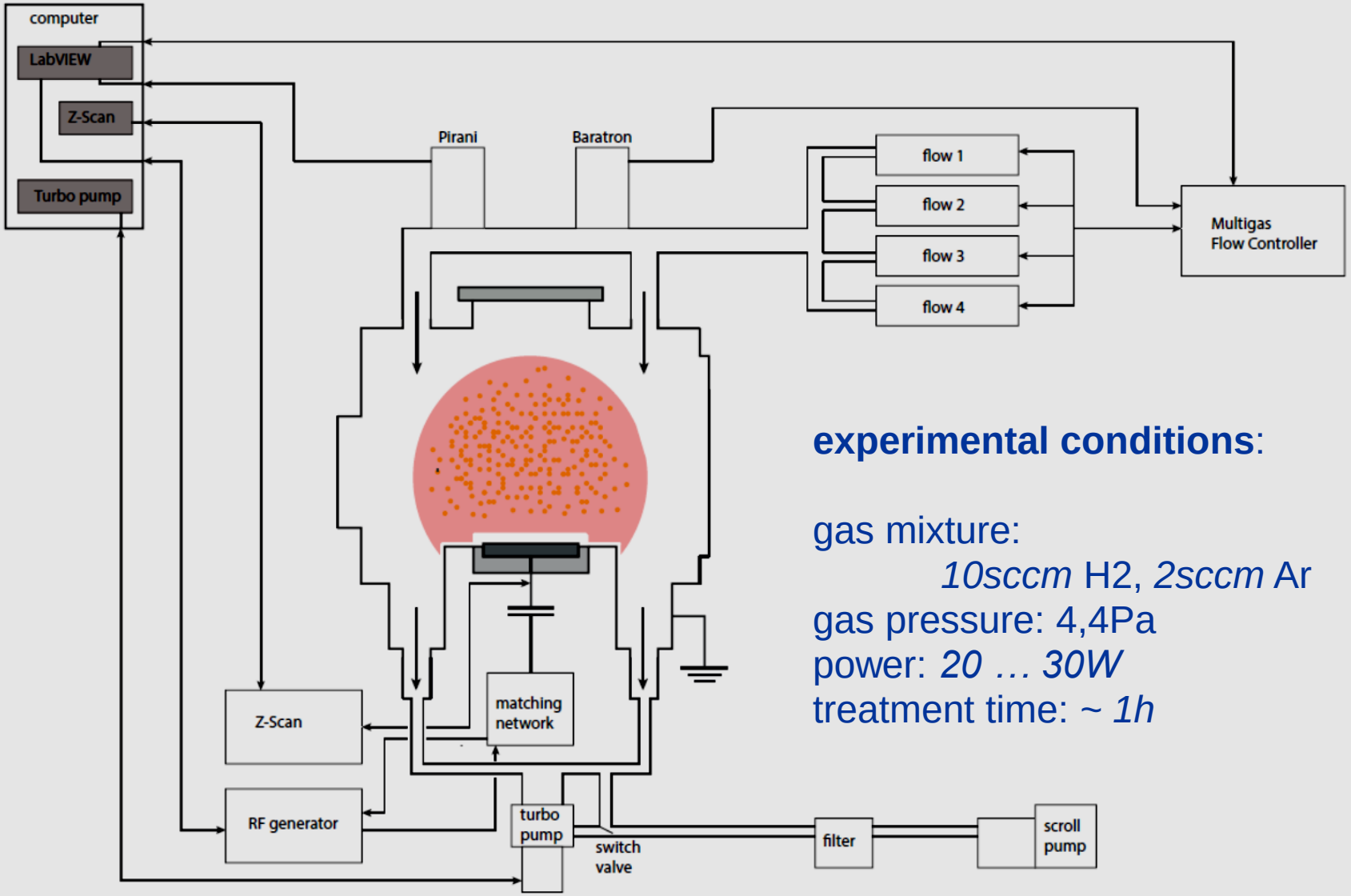



*Hinz, A., von Wahl, E., Faupel, F. Strunskus, T., Kersten, H., Eur. Phys. J. D* ***72****(2018), 91.*

*Röpcke,J., Loffhagen,D., von Wahl,E., Nave,A.S.C., Hamann,S., van Helden,J.H., Lang,N., Kersten,H., Eur. Phys. J. D* ***72****(2018), 87.*

# plasma cleaning of daguerreotypes

rf plasma




**experimental conditions**:

gas mixture:
*10sccm* H2, *2sccm* Ar
gas pressure: 4,4Pa
power: *20 … 30W*
treatment time: *~ 1h*

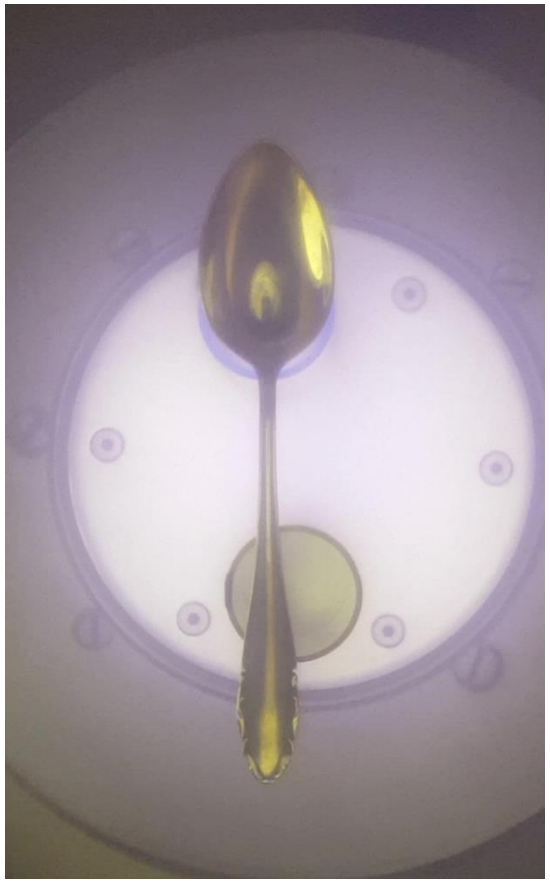
# plasma cleaning of daguerreotypes



## test with silver spoon

before

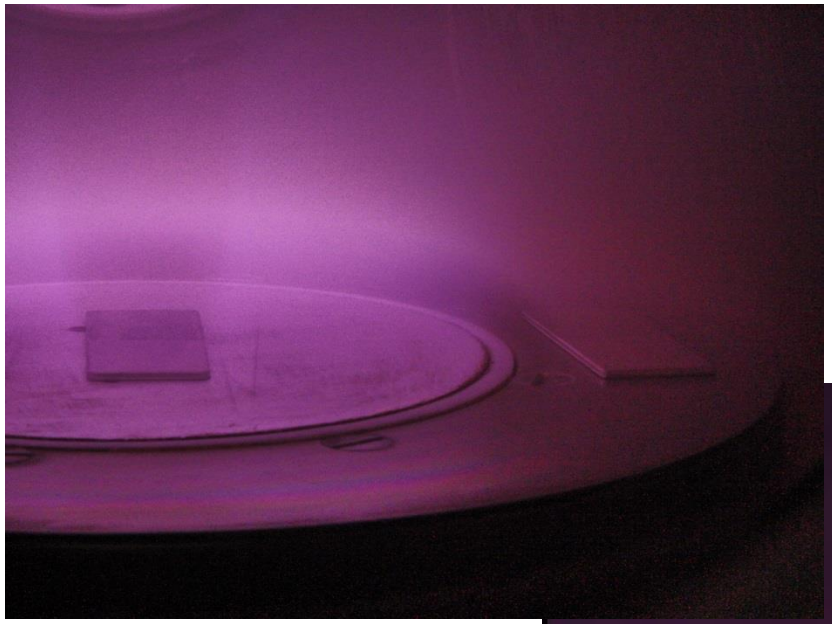
treatment time of 45 min



after

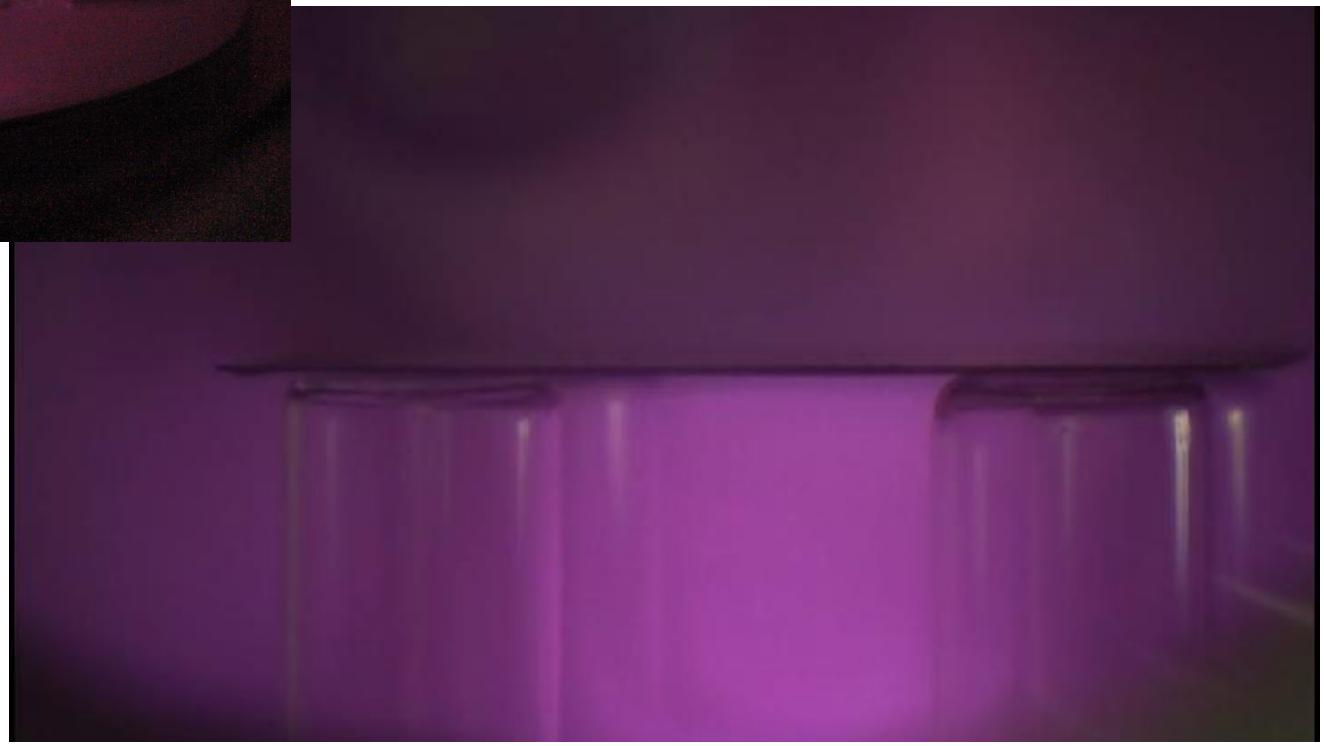
# plasma cleaning of daguerreotypes

rf plasma



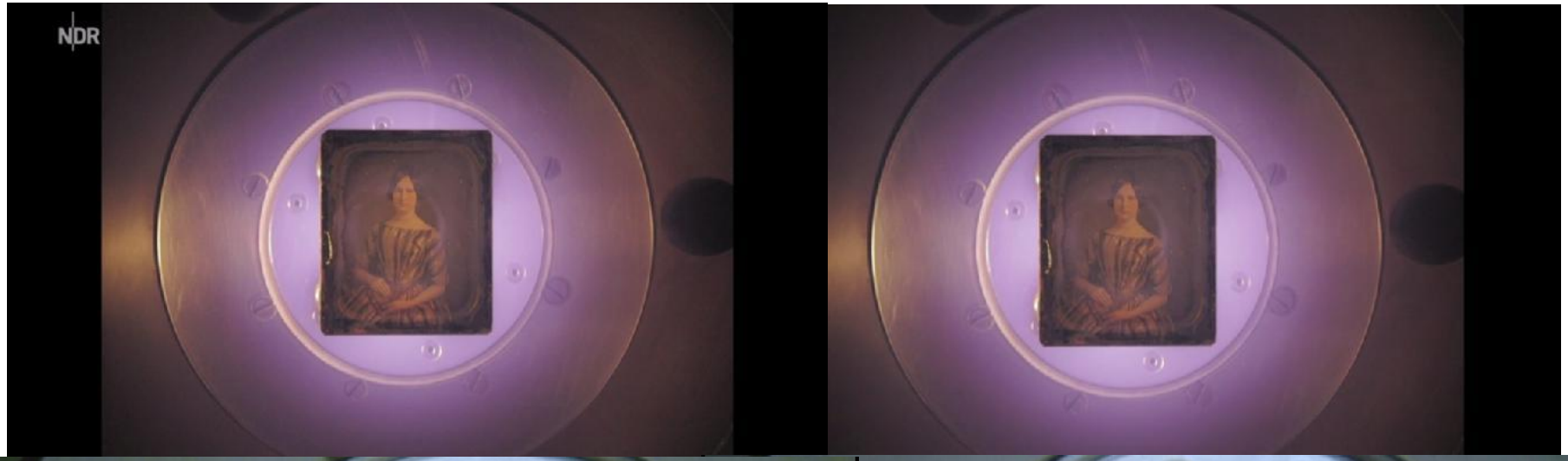
direct plasma treatment (electrode)

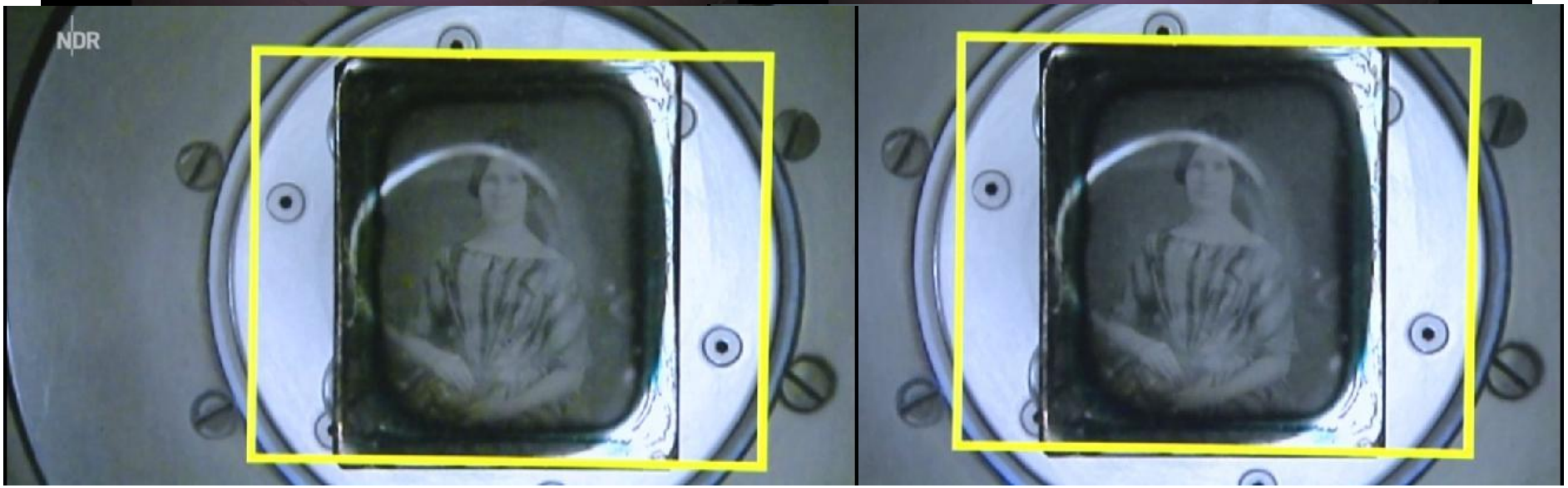
afterglow plasma treatment (floating substrate)



# plasma cleaning of daguerreotypes

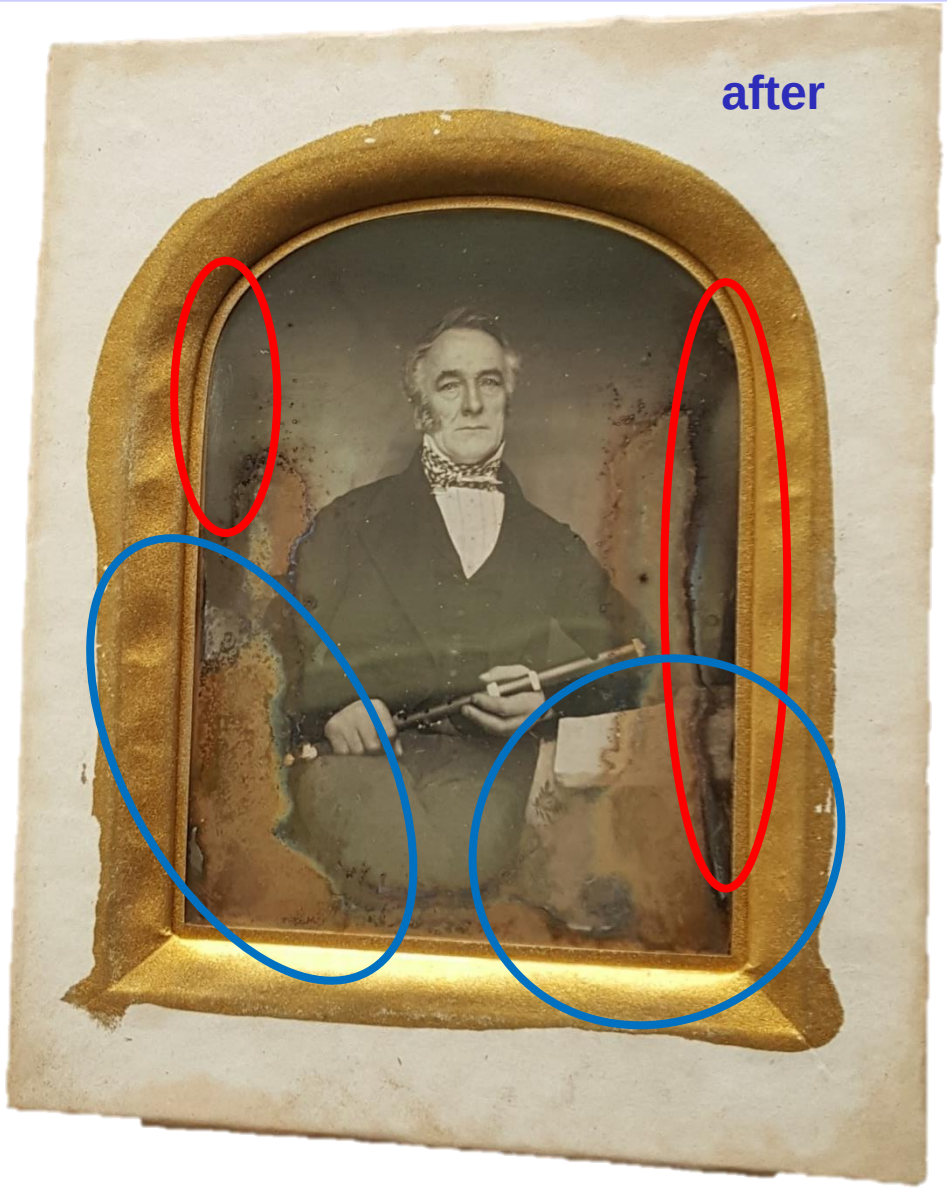
results



# plasma cleaning of daguerreotypes

results

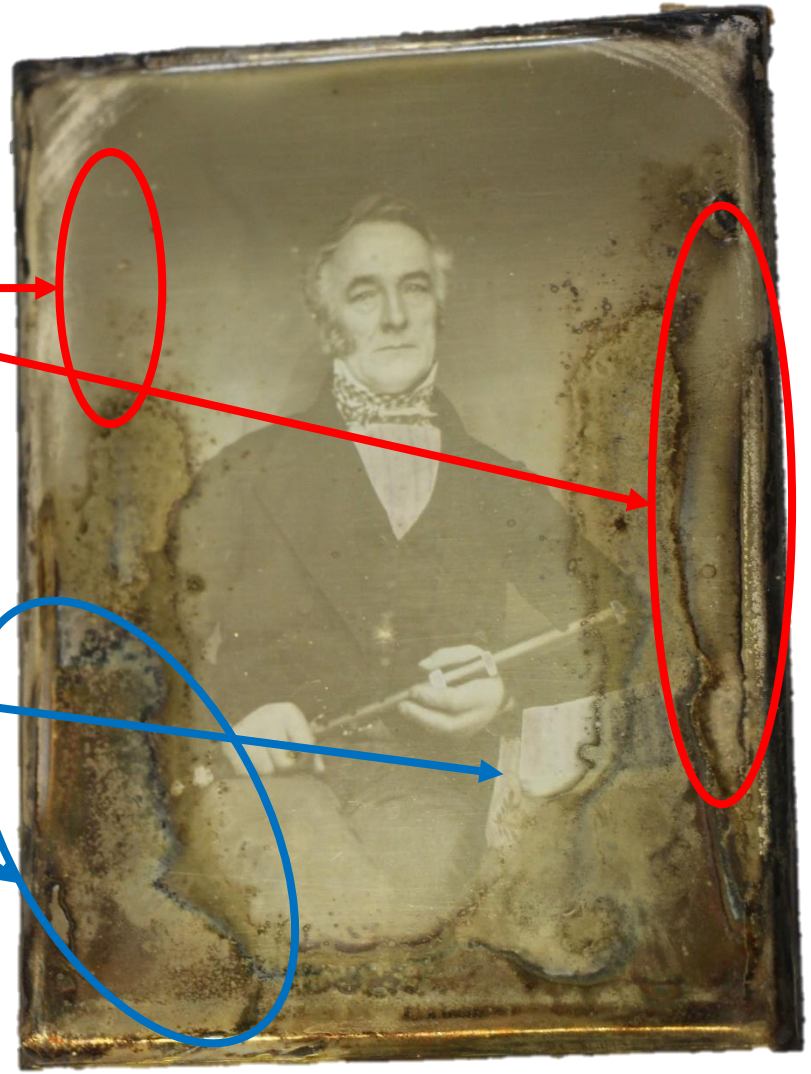



# plasma cleaning of daguerreotypes

results

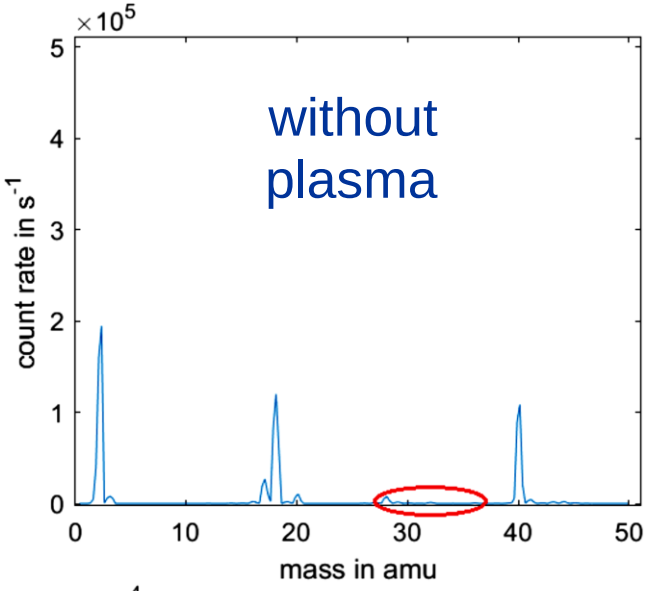
- treatment time: 30 min
- dark layers by silver sulfide could be removed
- in total, the surface of the photoraph became remarkably brighter

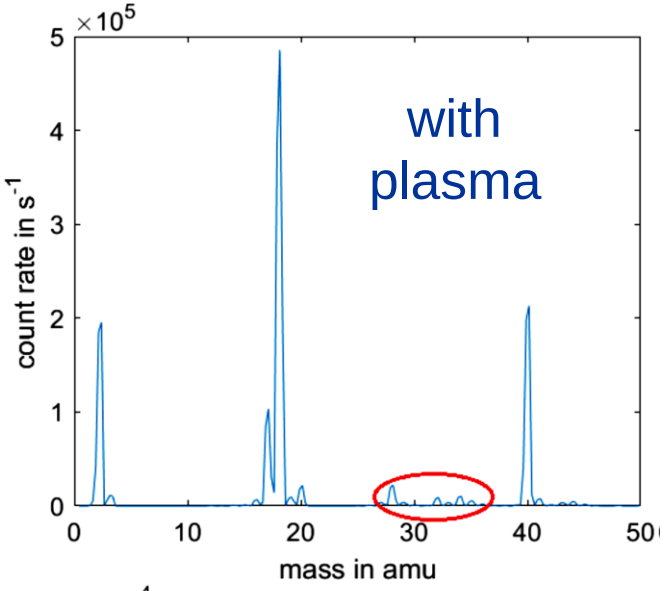
- no changes at the back side
- light change of colour by plasma treatment due to chemical reactions with other species at the surface

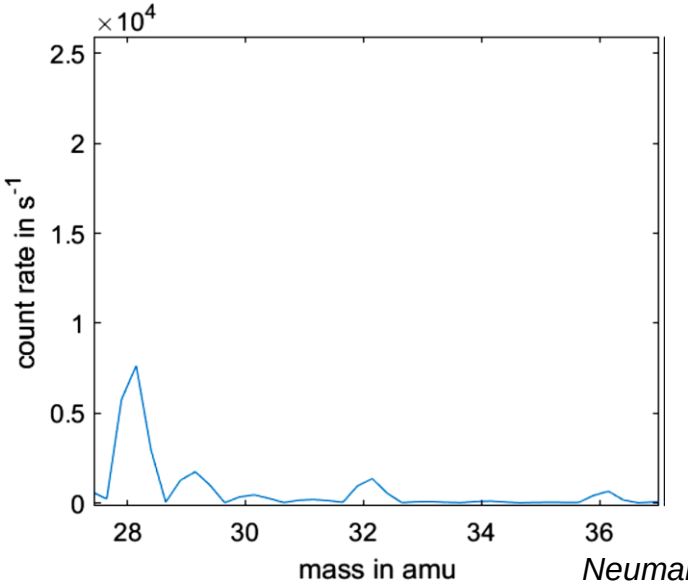


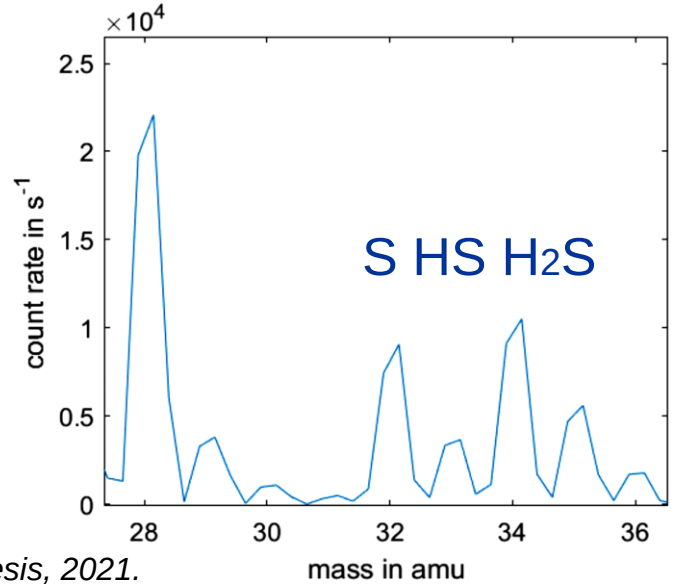
# plasma cleaning of daguerreotypes

results, MS




*Neumann, K., BSc thesis, 2021.*

# plasma cleaning of daguerreotypes

results

before

after

*Renard, B., Photo Antiquaria,* ***119****(2014), 8-10.*
*Renard, B., Photographica Cabinett,* ***61****(2014), 62-64.*

# plasma cleaning of daguerreotypes

results

# plasma cleaning of daguerreotypes

results

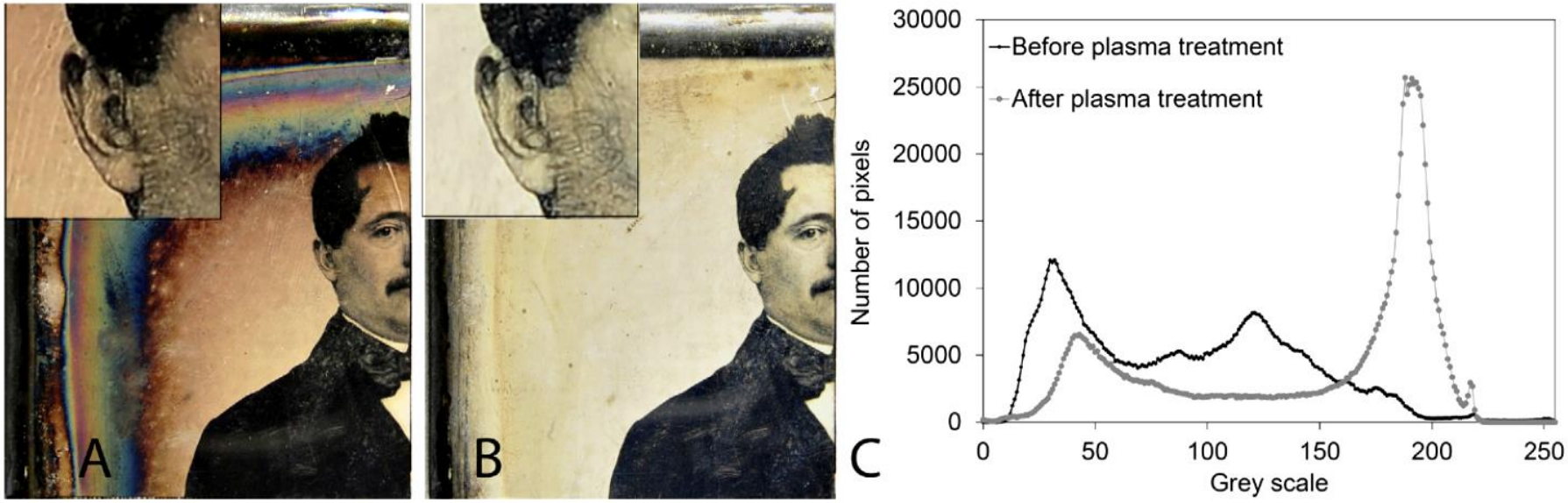


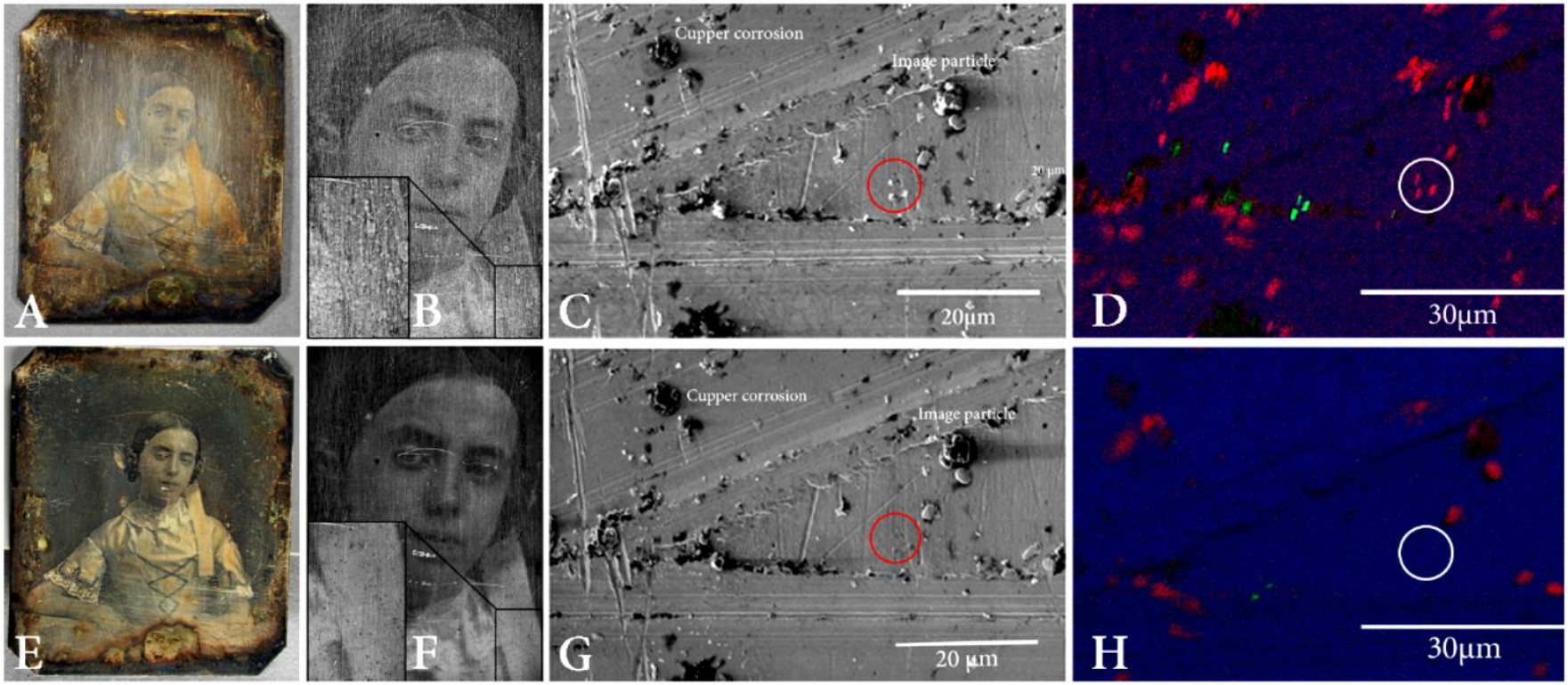

**Fig. 7.** A. Colour macro-photos collected from the same position under exact the same illumination conditions before and after plasma treatment of case 2. B. Colour image after plasma treatment. C. Histogram of the grey scale images of overall image.

*Grieten, E., Schalm, O., Tack, P., Bauters, S., Storme, P., et.al., J. Cultural Heritage,* ***28****(2017), 56-64.*

- effect of afterglow plasma treatment shows that there is an **overall visual improvement**
- dark zone become somewhat brighter, while the light grey zones become considerably brighter
- larger distance betwen both peaks result in an enhanced contrast
- the object is **shinier or cleaner after treatment**

# plasma cleaning of daguerreotypes

results



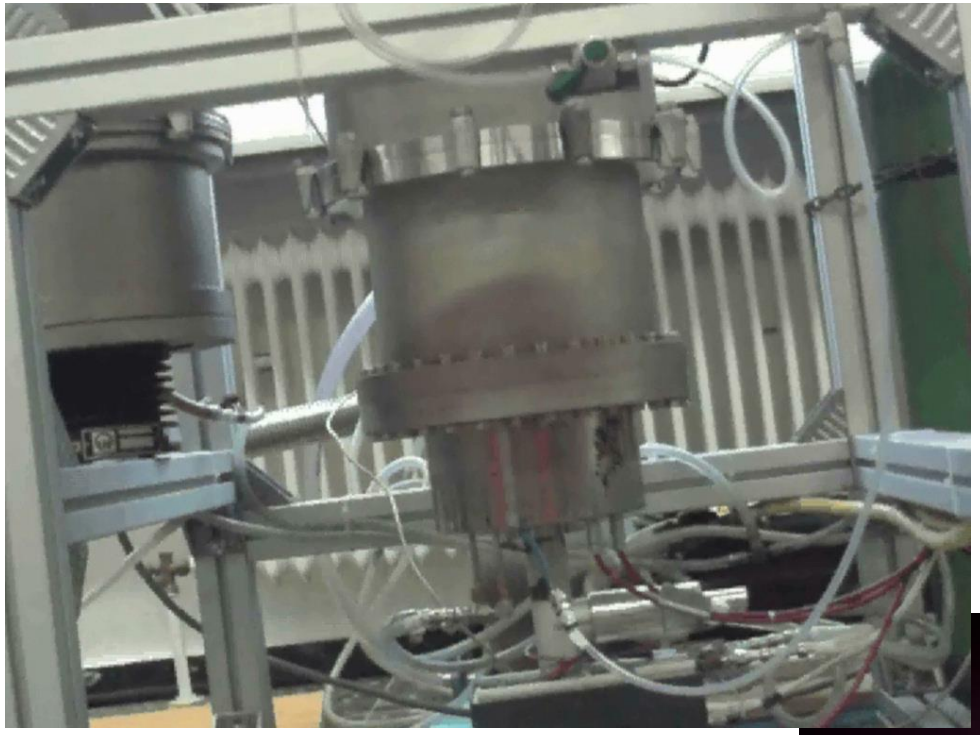

*Grieten, E., Schalm, O., Tack, P., Bauters, S., Storme, P., et.al., J. Cultural Heritage,* ***28****(2017), 56-64.*

# plasma cleaning of other artefacts



# plasma cleaning of other artefacts

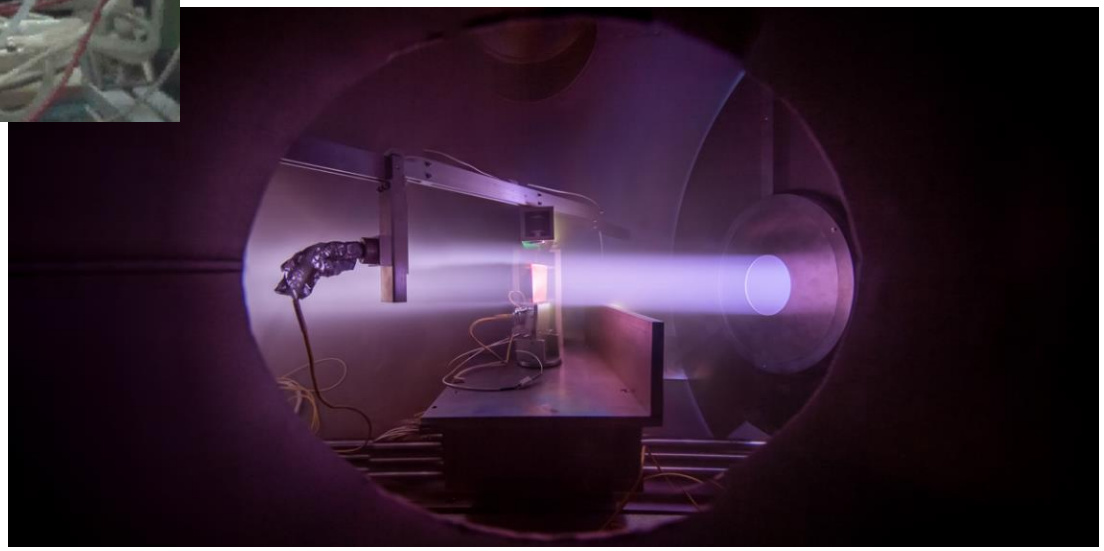
## ion beam etching



*courtesy: T. Brandt*

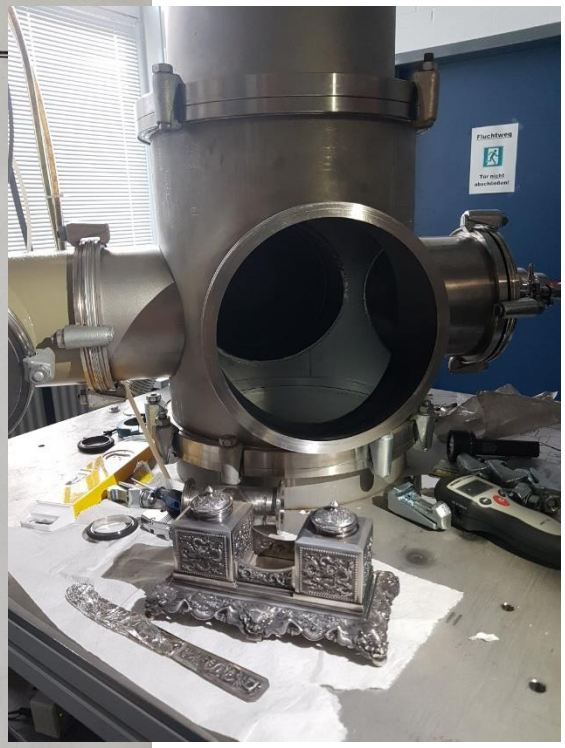
***VIBEx***

***HIBEx***



# plasma cleaning of other artefacts

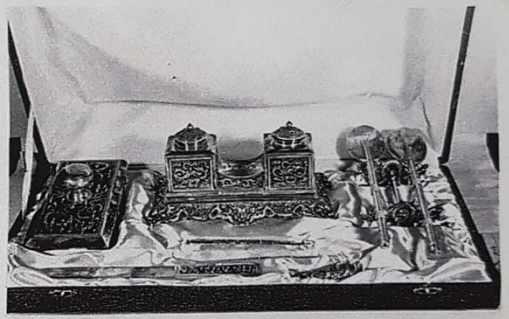
## ion beam etching



Hauptkatalog SAs 15121 a-h | Jahr und Nr. der Sendung 1956/22 | Original-Nr. 1139

Volk

Örtlichkeit Vietnam



Von wem gesammelt Geschenk der Volksrep. Vietnam an Präsident Wilh. Pieck

Von wem erhalten Präsidialkanzlei

Art der Erwerbung ü

GRASSI Museum
für Völkerkunde
Leipzig

# plasma cleaning of other artefacts

## ion beam etching

solid pieces

# Plasmareinigung

## Plasmareinigung von Kunstgegenständen im Ionenstrahl

Fotos: Leander Marxen und GrassiMuseum Leipzig

# summary

# summary

- **plasma treatment** (rf glow discharge) is a reliable method for restoration and conservation of daguerreotypes
- similartities to **plasma cleaning** (experiences)
- example: restoration / cleaning of surfaces in a **hydrogen-containing non-thermal low-pressure plasma (rf discharge) in afterglow (floating)** for reduction of silver sulfide (corrosive contaminations)
- in addition to restoration / cleaning, **conservation / protective coating** of daguerreotypes is possible, too
- **atmospheric pressure plasmas** become increasing importance
- **interest ???** kersten@physik.uni-kiel.de