Chapter 21

Laboratory-Scale Soft X-ray Source for Microscopy and Absorption Spectroscopy

Matthias Müller and Klaus Mann

Abstract Soft X-ray microscopy and absorption spectroscopy are extremely useful tools for high-resolution imaging and chemical analysis of samples in various scientific fields. However, due to the required high photon flux of soft X-ray radiation, up to now, both methods are almost exclusively performed at synchrotron sources. Thus, great efforts have been made to develop table-top sources emitting in the soft X-ray spectral range ($\lambda = 1\text{--}5\text{ nm}$). Here, the development of a laser-produced plasma source from a pulsed gas jet is presented, enabling the construction of an almost debris-free, compact and long-term stable X-ray source. Based on this source a compact soft X-ray microscope (spatial resolution 50 nm) operating at a wavelength of $\lambda = 2.88\text{ nm}$ was built and applied for imaging of various test and biological objects. In addition, a laboratory-scale NEXAFS spectrometer has been established, allowing for reliable analysis of different absorption edges at photon energies between 250 and 1250 eV.

PACS Subject Classification: 07.85.Fv · 07.85.Nc · 07.85.Tt · 32.30.Rj · 52.38.Ph · 52.50.Dg · 52.50.Jm. 61.10.Ht · 68.37.Yz. 78.70.Dm

21.1 Table-Top Soft X-ray Source Using a Pulsed Gas Jet

The laser-produced plasma source for the generation of intense soft X-ray radiation is based on a gas-puff target and a Nd:YAG laser system (wavelength $\lambda = 1064\text{ nm}$, pulse energy 700 mJ, pulse width 7 ns, repetition rate 5 Hz) as schematically depicted in Fig. 21.1. The radiation characteristics depend strongly on the gases used (see Fig. 21.3a, b): Photon emission spectra of low atomic number gases (e.g. oxygen and nitrogen) consist of individual, isolated lines, whereas those of gases

M. Müller · K. Mann (✉)

Laser-Laboratorium Göttingen e.V., Hans-Adolf-Krebs-Weg 1, 37077 Göttingen, Germany
e-mail: kmann@llg-ev.de

M. Müller

e-mail: matthias.mueller@llg-ev.de

© The Author(s) 2020

T. Salditt et al. (eds.), *Nanoscale Photonic Imaging*, Topics in Applied Physics 134,
https://doi.org/10.1007/978-3-030-34413-9_21

549

Fig. 21.1 Schematic drawing (left) and photograph (right) of the table-top laser-produced soft X-ray plasma source at Laser-Laboratorium Göttingen

with a high atomic number (argon, krypton, xenon) are quasi-continuous due to the higher number of possible electronic transitions.

The pulsed gas jet is created by a conical nozzle (diameters $d_1 \approx 550 \mu\text{m}$, $d_2 \approx 300 \mu\text{m}$, cone half angle 7°) behind a fast valve. The latter is based on the Proch-Trickl setup [1], consisting of a piezo disk translator to generate short gas pulses ($t_{\text{open}} = 900 \mu\text{s}$), allowing for a background pressure of about $5 \cdot 10^{-3}$ mbar during operation (gas pressure $p = 10\text{--}20$ bar).

As compared to alternative laser-produced plasma sources employing solid or liquid targets, the gas jet based source offers several advantages. In particular, these are:

- Low debris generation, i.e. cleanliness,
- Continuous supply of target material,
- Long-term stability.

However, due to the reduced particle density of the gas jet, the peak brilliance is definitely smaller as the plasma size increases to several hundreds of micrometer. Progress in the enhancement of gas density has been achieved by using cluster beam targets [2] or double-stream gas puff targets [3]. Another successful approach is the generation of a so-called “barrel shock”, applying a small background pressure p_b to the supersonic flow emanating from the nozzle ([4], see Fig. 21.2a). On passing this barrel shock system, particles become locally concentrated, forming high-density regions. Focusing the laser beam into the high-density region behind one of these shocks, a higher number of gas atoms can be ionized, resulting in a brighter and smaller plasma (see Fig. 21.2b). The peak brilliance of the source is increased by one order of magnitude to $3.15 \cdot 10^{16}$ photons/(mm² mrad s) for the isolated nitrogen line at $\lambda = 2.88$ nm.

The emission characteristics of a soft X-ray plasma are not only affected by the target gas and its particle density, but also by the laser parameters. The influence of the laser pulse length was investigated, employing two lasers of about the same pulse energy (500 mJ, $\lambda = 1064$ nm), but with different pulse durations of 7 ns and 170 ps [5]. As seen from the compilation in Fig. 21.3, the spectral characteristics of the plasma emission are clearly affected by the pulse duration (i.e. power density): The

Fig. 21.2 **a** Schematic representation of the plasma generation in a “barrel shock”: The local confinement of target gas atoms by an X-ray transparent background gas (He, $p_b > 10$ mbar) allows for a plasma ignition at a greater distance from the nozzle as compared to the standard expansion into vacuum ($p_b < 10^{-4}$ mbar). **b** Pinhole camera images indicating plasma intensities at $\lambda = 2.88$ nm, superimposed on Schlieren images of the gas jet under vacuum conditions and in an ambient He atmosphere, respectively [4]

Fig. 21.3 Influence of laser pulse duration on emission spectra of **a** nitrogen and **b** krypton from both ns (red) and ps (blue) laser plasmas (target gas pressure 10 bar, 200 nm Al-filtered, average of 100 pulses). **c** Comparison of measured and calculated argon emission spectra for ns and ps laser and corresponding pinhole camera images [5]

brightness is strongly enhanced, for some emission lines by more than a factor of 10. The picosecond spectra are shifted considerably towards shorter wavelengths since the higher power density results in a higher degree of ionization.

By comparing the spectra with model calculations using a magneto-hydrodynamic code electron temperatures and densities were obtained, indicating the maximum achievable degree of ionization of the plasma. As an example, Fig. 21.3c shows measured and calculated emission spectra of the argon plasma for both ns and ps laser excitation. The average electron temperature resulting from the simulation is 66

Fig. 21.4 Pinhole camera images of krypton plasma (average 100 pulses) taken at 90° and 30° to the incident laser beam

eV for the ps plasma (33% larger than for ns), whereas the electron density is about 3 times higher ($22.4 \cdot 10^{19}$ eV/cm³). Along with the higher degree of excitation, the ps laser-produced plasmas are also considerably smaller, as could be monitored with a soft X-ray sensitive pinhole camera (see Fig. 21.3c inset).

Recent investigations on the angular emission characteristics of the laser-produced plasma have demonstrated that the emission of soft X-rays in backward direction is strongly favored. This can be explained by a shorter path length and thus, a reduced reabsorption of the radiation by the gas jet in direction of the laser beam. The plasma intensity is enhanced by a factor of 1.6 when the emitted soft X-ray radiation is utilized under an angle of 30° with respect to the incoming laser beam, as compared to the previously chosen 90° geometry (see Fig. 21.4). In addition, the effective irradiation area of the plasma becomes 4x smaller, and the positional stability of the source is increased by a factor of 5.

21.2 Soft X-ray Microscopy

Benefiting from the high absorption contrast between carbon and oxygen, transmission X-ray microscopy in the spectral range of the “water window” ($\lambda = 2.3\text{--}4.4$ nm) is ideally suited for the investigation of biological samples. Using Fresnel zone plates as highly magnifying objectives spatial resolutions in the range of 10 nm have been achieved at synchrotron sources [6]. However, in order to pave the way for a wider dissemination of soft X-ray microscopy, there is definitely also the need for table-top systems. Although considerable progress has already been achieved in this field [7–10], a further compaction and simplification of these microscopes is still necessary.

Making use of the long-term stable and nearly debris-free laser-produced plasma from a pulsed nitrogen gas jet target, an extremely compact soft X-ray microscope operating in the “water window” region at the wavelength $\lambda = 2.88$ nm was installed and tested [11, 12]. The setup of this table-top soft X-ray microscope is depicted in Fig. 21.5a. It consists basically of the laser-produced plasma source described in Sect. 21.1, an ellipsoidal condenser mirror, a Fresnel zone plate objective fabricated by standard lithographic techniques, and a back-illuminated CCD camera sensitive for soft X-ray radiation, all integrated into a vacuum system with a base pressure of 10^{-6} mbar.

The soft X-ray radiation emitted from the nitrogen plasma is filtered by a titanium (Ti) filter to block out-of-band radiation, ensuring monochromatic irradiation of

Fig. 21.5 **a** Photograph of the table-top soft X-ray microscope. **b** Spatial intensity profiles of soft X-ray radiation at $\lambda = 2.88$ nm for different positions along the optical axis behind the ellipsoidal condenser mirror; the minimum spot diameter at $z = 0$ mm (object plane) is about $400\text{ }\mu\text{m}$ (FWHM). **c–f** Soft X-ray micrographs of **c** Siemens star, **d** geo-colloids, **e** bacterium *Deinococcus Radiodurans* (DSM no. 20539) and **f** alga *Trachelomonas oblonga* (SAG 1283-11). Magnification and exposure time vary from 175 to 500 and 5 min to 60 min, respectively. **a**, **e**, **f** reproduced from [12], with permission of AIP Publishing. **d** reprinted with permission from [11], Optical Society of America

the sample at $\lambda = 2.88$ nm wavelength. The adjustment of the grazing incidence condenser mirror was optimized by the measurement of intensity profiles at various positions along the optical axis. Figure 21.5b displays corresponding distributions for different camera positions. A Gaussian-like spatial profile with a diameter of about $400\text{ }\mu\text{m}$ (FWHM) is measured at the focal plane, representing the object plane of the soft X-ray microscope.

In order to assess the performance of the microscope a Siemens star test pattern was imaged. Figure 21.5c shows a corresponding micrograph, indicating an almost uniform illumination over a field of view of about $10\text{ }\mu\text{m}$. Structures with a size of about 50 nm are resolved in all directions [12]. Furthermore, various biological and geological samples were investigated (see Fig. 21.5d, e). The characteristic shape of these objects is clearly visible, but almost no internal structure is apparent due to the thickness of the samples. The signal-to-noise ratio of the micrographs is rather low due to the relatively low brilliance of the plasma. However, the presented system offers various opportunities for scalability of the photon flux (see Sect. 21.1), thereby maintaining the compactness of the microscope and especially the inherent cleanliness of the soft X-ray source.

21.3 X-ray Absorption Spectroscopy

Another prominent application of soft X-ray radiation is absorption spectroscopy, probing the fine structure of X-ray absorption edges (Near Edge X-ray Absorption Fine Structure—NEXAFS), by exciting core level electrons to higher lying unoccu-

Fig. 21.6 Schematic representation (top) and photograph (bottom) of the laboratory-scale NEXAFS spectrometer

pled states. As the energy levels of both initial and final states depend on the involved molecular bonds and their chemical environment, the spectral features of the near-edge fine structure represent a “molecular fingerprint” of the sample. Thus, NEXAFS spectroscopy is a very common analytical method for compositional surface analysis, representing nowadays one of the most important applications of synchrotron radiation [13]. In contrast to soft X-ray microscopy, however, it has been conducted only a few times with laboratory-scale sources until now [14–17], although almost identical results as with radiation from storage rings are achievable.

At the Laser-Laboratorium Göttingen (LLG) a compact spectrometer based on the laser-produced soft X-ray plasma source was developed and utilized for NEXAFS measurements. Figure 21.6 shows the current setup of the table-top spectrometer, which makes use of a concave flat-field grating and a soft X-ray sensitive CCD camera. At synchrotrons absorption spectroscopy is conducted mainly by recording the total electron yield using monochromatic radiation for excitation. In contrast, the broadband radiation emitted from lab-scale sources allows for a polychromatic spectroscopic approach.

Up to now, a considerable number of NEXAFS investigations has been performed at the soft X-ray absorption edges of various elements. A brief overview of the spectra measured so far at the carbon K-edge is given in Fig. 21.7a, showing polyimide [16], humic substances and the organic matter of a Luvisol [18]. Differences in spectral features point out varying influences of e.g. aromatic, phenolic, and carbonyl functional groups.

Fig. 21.7 NEXAFS spectra acquired at various absorption edges with the compact spectrometer at LLG: **a** C K-edge spectra of polyimide, humic acid, fulvic acid and a luvisol bulksoil [19], **b** Cl L-edge spectrum of NaCl [20] indicating EXAFS oscillations, in comparison with corresponding synchrotron results [21], **c** overview spectrum of PCMO [22], **d** O K-edge and Mn L-edge spectra of various Mn compounds [23] and **e** O K-edge and Fe L-edge spectra of hematite samples of different thickness

Furthermore, NEXAFS studies were conducted at the absorption edges of Si, S, Cl (see Fig. 21.7b, [20]), Ca [24], O [22, 23], and, for the first time with a laboratory-scale setup, at the L-edges of Mn, Fe and Cu [22, 23, 25] at photon energies >500 eV (Fig. 21.7c–e). In all cases, there is an excellent agreement of spectral features compared to spectra obtained with synchrotron radiation. The energy resolution of the spectrometer is about $E/\Delta E \approx 450$ at a photon energy of 430 eV. However, a higher

spectral resolution is necessary, e.g. for the analysis of Fe oxides to resolve the underlying splitting of the pre-edge features around 530 eV and the $L_{3,2}$ peaks between 700 and 725 eV.

Besides the investigation of different absorption edges, the soft X-ray source was applied for time-resolved NEXAFS measurements in Perovskite-type manganite $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO). Pump-probe experiments reveal diminutive changes of the oxygen K-edge, stemming from an optically induced phase transition [22], which compare nicely to synchrotron data [26].

Due to the short mean free path of soft X-rays in air (only a few millimeters), NEXAFS experiments with the table-top spectrometer have so far been performed in a high vacuum system, excluding a number of interesting samples from spectroscopic investigations. To overcome this limitation, a new sample chamber was constructed using two silicon nitride membranes as vacuum windows (see Fig. 21.8a and b) to measure samples also under atmospheric conditions.

NEXAFS spectra have been recorded under different conditions in this sample chamber, i.e. vacuum, air and helium, respectively, on e.g. the calcium L-edge and oxygen K-edge of crystalline calcium chloride tetra- or hexahydrate [25]. Obviously, NEXAFS measurements are feasible for all conditions at the calcium L-edge (see Fig. 21.8c). However, the oxygen signal is absent in vacuum and air (see Fig. 21.8d). During measurement in vacuum, the crystalline structure is changing along with the decreasing atmospheric pressure from a tetra- or hexahydrate into a water-free distorted “rutile-structure” [27], thus no traces of water are detected. In air, these hydrate structures are still present, but could not be measured due to the strong absorption above the nitrogen K-edge. Therefore, helium purging turns out to be essential for the proper investigation of sensitive samples.

Fig. 21.8 **a** Drawing and **b** photograph of the helium purged sample chamber. **c** Ca L-edge and **d** O K-edge spectra of $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ recorded for different conditions. Reproduced from [25], with the permission of the American Vacuum Society

21.4 Outlook

At present state, NEXAFS studies with the table-top spectrometer are conducted in transmission mode, requiring very thin samples (≈ 100 nm). Experiments in reflection geometry would also allow for investigation of thick samples, which cannot be prepared for measurements in transmission. Additionally, taking advantage of the short penetration depth of soft X-rays under grazing incidence (< 30 nm), measurements in reflection would yield highly surface sensitive information. Thus, the setup shall be modified to accomplish NEXAFS experiments both in transmission and reflection mode.

The soft X-ray microscope shall be extended to a STED integrated X-ray nanoscope. Combining both methods allows for comprehensive studies of biological objects due to the complementary contrast of both imaging techniques. Thus, in addition to pure imaging of the sample also information about its chemical composition can be gained without transferring the sample between different setups.

Moreover, the table-top EUV source can be used for metrological applications at the microlithographic wavelength $\lambda = 13.5$ nm, e.g. for material testing or actinic sensor qualification.

References

1. Proch, D., Trickl, T.: A high-intensity multi-purpose piezoelectric pulsed molecular beam source. *Rev. Sci. Instrum.* **60**(4), 713–716 (1989)
2. Kubiak, G., Richardson, M.: US Patent 5,577,092 (1996)
3. Fiedorowicz, H., Bartnik, A., Daido, H., Choi, I., Suzuki, M., Yamagami, S.: Strong extreme ultraviolet emission from a double-stream xenon/helium gas puff target irradiated with a Nd:YAG laser. *Opt. Commun.* **184**(1–4), 161–167 (2000)
4. Mey, T., Rein, M., Großmann, P., Mann, K.: Brilliance improvement of laser-produced soft x-ray plasma by a barrel shock. *New J. Phys.* **14**(7), 073045 (2012)
5. Müller, M., Kühl, F.-C., Großmann, P., Vrba, P., Mann, K.: Emission properties of ns and ps laser-induced soft x-ray sources using pulsed gas jets. *Opt. Express* **21**(10), 12831 (2013)
6. Chao, W., Fischer, P., Tylliszczak, T., Rekawa, S., Anderson, E., Naulleua, P.: Real space soft x-ray imaging at 10 nm spatial resolution. *Opt. Express* **20**(9), 9777–9783 (2012)
7. Berglund, M., Rymell, L., Peuker, M., Wilhein, T., Hertz, H.: Compact water-window transmission x-ray microscopy. *J. Microsc.* **197**(3), 268–273 (2000)
8. Jansson, P., Vogt, U., Hertz, H.: Liquid-nitrogen-jet laser-plasma source for compact soft x-ray microscopy. *Rev. Sci. Instrum.* **76**, 043503 (2005)
9. Legall, H., Blobel, G., Stiel, H., Sandner, W., Seim, C., Takman, P., Martz, D., Selin, M., Vogt, U., Hertz, H., Esser, D., Sipma, H., Luttmann, J., Höfer, M., Hoffmann, H., Yulin, S., Feigl, T., Rehbein, S., Guttmann, P., Schneider, G., Wiesemann, U., Wirtz, M., Diete, W.: Compact x-ray microscope for the water window based on a high brightness laser plasma source. *Opt. Express* **20**(16), 18362–18369 (2012)

10. Takman, P.A., Stollberg, H., Johansson, G.A., Holmberg, A., Lindblom, M., Hertz, H.M.: High-resolution compact x-ray microscopy. *J. Microsc.* **226**(2), 175–181 (2007)
11. Müller, M., Mey, T., Niemeyer, J., Mann, K.: Table-top soft x-ray microscope using laser-induced plasma from a pulsed gas jet. *Opt. Express* **22**(19), 23489 (2014)
12. Müller, M., Mey, T., Niemeyer, J., Lorenz, M., Mann, K.: Table-top soft x-ray microscopy with a laser-induced plasma source based on a pulsed gas-jet. *AIP Conf. Proc.* **1764**, 030003 (2016)
13. Stöhr, J.: *NEXAFS spectroscopy*. Springer, Berlin (2003)
14. Przemyslaw, W., Duda, M., Bartnik, A., Sarzynski, A., Wegrzynski, L., Nowak, M., Jancarek, A., Fiedorowicz, H.: Compact system for near edge X-ray fine structure (NEXAFS) spectroscopy using a laser-plasma light source. *Opt. Express* **26**(7), 8260–8274 (2018)
15. Mantouvalou, I., Witte, K., Grötzsch, D., Neitzel, M., Günther, S., Baumann, J., Jung, R., Stiel, H., Kanngießer, B., Sandner, W.: High average power, highly brilliant laser-produced plasma source for soft X-ray spectroscopy. *Rev. Sci. Instrum.* **86**, 035116 (2015)
16. Peth, C., Barkusky, F., Mann, K.: Near-edge x-ray absorption fine structure measurements using a laboratory-scale XUV source. *J. Phys. D Appl. Phys.* **41**(10), 105202 (2008)
17. Vogt, U., Wilhein, T., Stiel, H., Legall, H.: High resolution x-ray absorption spectroscopy using a laser plasma radiation source. *Rev. Sci. Instrum.* **75**, 4606 (2004)
18. Sedlmair, J., Gleber, S.-C., Peth, C., Mann, K., Niemeyer, J., Thieme, J.: Characterization of refractory organic substances by NEXAFS using a compact X-ray source. *J. Soils Sediments* **12**, 24–34 (2012)
19. Sedlmair, J.: *Soft x-ray spectromicroscopy of environmental and biological samples*. Ph.D. thesis, Universität Göttingen (2011)
20. Olschewski, M.: *Aufbau und Charakterisierung eines Absorptions- und Reflektionsspektrometers für den EUV-Bereich unter Verwendung eines laserinduzierten Plasmas*. Master's thesis, TU Clausthal (2012)
21. Kasrai, M., Fleet, M., Bancroft, G., Tan, K., Chen, J.: X-ray-absorption near-edge structure of alkali halides: the interatomic-distance correlation. *Phys. Rev. B* **43**(2), 1763–1772 (1991)
22. Großmann, P., Rajkovic, I., More, R., Norpoth, J., Techert, S., Jooß, C., Mann, K.: Time resolved near-edge X-ray absorption fine structure spectroscopy on photo-induced phase transitions using a tabletop soft-X-ray spectrometer. *Rev. Sci. Instrum.* **83**, 053110 (2012)
23. Schellhorn, M.: *Präparation von Probensystemen pedochemisch relevanter Metallverbindungen zur Untersuchung durch ein tabletop Röntgen-Nahkanten Spektrometer*. Master's thesis, Universität Hohenheim (2015)
24. Kühl, F.-C.: *Nah-Kanten-Absorptionsspektroskopie im weichen Röntgenbereich bei Atmosphärendruck*. Bachelor's thesis, HAWK Göttingen (2013)
25. Kühl, F.-C., Müller, M., Schellhorn, M., Mann, K., Wieneke, S., Eusterhues, K.: Near edge X-ray absorption fine structure spectroscopy at atmospheric pressure with a table-top laser-induced soft X-ray source. *J. Vac. Sci. Technol. A* **34**, 041302 (2016)
26. Rini, M., Zhu, Y., Wall, S., Tobey, R.-I., Ehrke, H., Garl, T., Freeland, J.-W., Tomioka, Y., Tokura, Y., Cavalleri, A., Schoenlein, R.-W.: Transient electronic structure of the photoinduced phase of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ probed with soft X-ray pulses. *Phys. Rev. B* **80**, 155113 (2009)
27. Galasso, F.S.: *Structure and properties of inorganic solids*. In: Kurti, N., Smoluchowski, R. (eds.) *International Series of Monographs in Solid State Physics*. Elsevier, Amsterdam (2013)

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.