# ZnO as Fast Scintillators Evaluated with Ni-like Ag Laser

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A nickel-like silver laser emitting at 13.9-nm wavelength was used to evaluate the scintillation properties of a hydrothermal method grown zinc oxide (ZnO) crystal in an extreme ultraviolet region. The streak images were used to study the temperature dependence and decay time of ZnO emission from 25 K to 298 K. Increasing the temperature within this range gradually the emission peak position from 3.32 eV to 3.22 eV. Additionally, its spectrum width in full width at half maximum increases by 0.09 eV from 0.05 eV (at 25 K) to 0.14 eV (at 298 K). Finally, the measured emission decay at 105 K was fitted by a double exponential decay to be $\tau_1$=0.88(4) ns, and $\tau_2$=2.7(2) ns. This decay time of a few nanoseconds is sufficiently short for the characterization of laser plasma EUV sources with nanoseconds duration and is suitable lithographic applications.

**Key Words**: Scintillator, X-ray laser, ZnO

## 1. Introduction

Optical technologies in the extreme ultraviolet (EUV) region have been receiving strong interest for next generation lithography applications.[1)] The development of suitable light sources and optical materials in this wavelength region plays an important role. In the past five years, efficient EUV light sources have been demonstrated.[2,3)] In addition, various efforts have also been made in the development of functional optical components. In particular, there is a need for the development of efficient and fast imaging scintillator devices with sufficient size since they are a key element for lithographic applications. In this aspect, hydrothermal method grown zinc oxide (ZnO) is a prominent candidate. Zinc oxide has been intensively studied for the past ten years as a light-emitting diode[4)] and as a nano-structured material with the aim of improving its optical properties including its response time.[5-7)] The advantage of bulk ZnO is the availability of large sized homogeneous crystals with a reasonable fabrication cost. Currently, its growth characteristics have been greatly improved in terms of crystalline quality and size. As an example, the growth of large sized crystals of up to 3-inch-diameter has recently been reported.[8)]

For the evaluation of hydrothermal method grown ZnO, a nickel-like silver EUV laser operating at 13.9 nm with a large pulse energy of up to micro-joules level and a sufficiently short pulse duration of several picoseconds is the ideal light source.[9,10)] Recently, the room temperature scintillation properties of ZnO in the EUV region using a nickel-like silver laser were demonstrated and a response time of a few nanoseconds was reported.[11)] In this paper, we present results on the temperature dependence of the ultraviolet emission of a ZnO crystal at 3.2 eV photon energy.

## 2. Experimental

The schematic diagram of the experimental setup is shown Fig. 1. The EUV laser operating at 13.9 nm was employed as the EUV excitation source. The lasing scheme is the 4*p*-4*d* transition of the nickel-like silver ion pumped with the transient collisional excitation.[9)] The two gain medium plasmas of the EUV laser were generated by irradiating flat silver targets with two laser pulses of a 1053 nm wavelength. The two pulses are separated by 2 ns, each having prepulse durations of 200 ps and main pulse durations of 3ps.[12)] The pulse energy of the EUV laser pulse was typically 500 nJ and

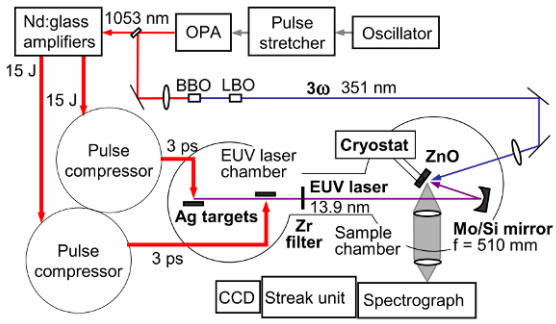


Fig.1 Schematic experimental setup for the evaluation of the scintillation properties of ZnO crystal with UV and EUV laser sources.

the duration was 7 ps. This single crystal ZnO sample is grown by hydrothermal method combined with a platinum inner container[4] and the sample was cut at a (0001) surface orientation. In order to measure its scintillation properties at different temperatures, the holder of ZnO crystal is connected to a temperature-controlled cryostat. The EUV laser was focused onto the sample using a molybdenum/silicon multilayer spherical mirror. In order to eliminate continuous emission from the silver plasma, a 0.2 μm zirconium foil was placed before the multilayer spherical mirror. The fluorescence spectrum and the fluorescence decay of the ZnO sample were measured using the 25 cm focal length spectrograph coupled with a streak camera. For comparison, the scintillation properties were also evaluated using the 351 nm third harmonics from the 1053 nm chirped pumping source for the EUV laser. The photon energy of the 351 nm excitation source is slightly higher than the band gap of the ZnO while its pulse duration is measured to be 110 ps.

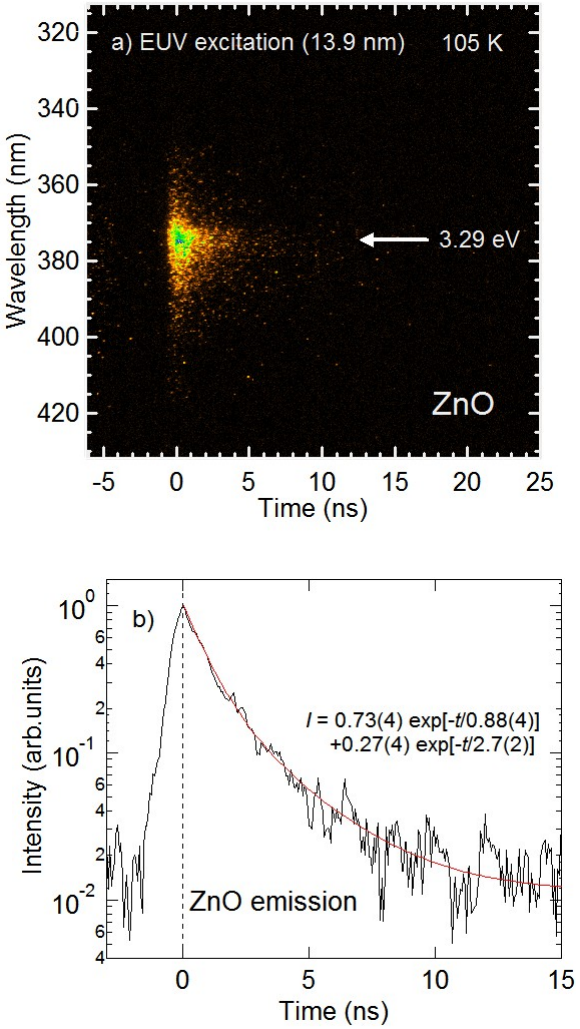


Fig.2 a) Spectrum-resolved streak image and b) temporal profile of the ZnO emission excited by EUV laser light (13.9 nm) at the sample temperature of 105 K. The temporal profile can be fitted by a double exponential decays function.

## 3. Results

**3.1** Spectrum-resolved Streak Image of ZnO Emission

The spectrum-resolved streak images of the emission from the ZnO excited by the EUV (13.9 nm) and UV (351 nm) excitation sources were measured for six different temperatures, namely; 298 K, 244 K, 192 K, 138 K, 105 K, and 25K. A representative spectrum-resolved streak image is shown in Fig.2 a), which was taken at 105 K temperature with the EUV laser as the excitation source. The spectral axis was calibrated using the UV excitation line since it is near the ZnO emission wavelength. The temporal decay profile at 105 K was obtained by integrating the streak camera data over the wavelength axis, as shown in Fig2 b). This temporal profile was fitted by a double exponential decay as described by

$$I=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2). \quad (1)$$

The fitting parameters were found to be $A_1$ = 0.73(3), $A_2$ = 0.27(4), $\tau_1$ = 0.88(4) ns, and $\tau_2$ = 2.7(2) ns. The presence of two decay constants were determined to be due to a fast decay time from the free exciton emission and a slow decay time, which is attributed to trapped carriers.[13] The corresponding temporal profile for the UV excitation case was also fitted by eq. (1) and the fitting parameters were $A_1$ = 0.66(7), $A_2$ = 0.41(7), $\tau_1$ = 0.81(6) ns, and $\tau_2$ = 2.4(3) ns. The temporal profiles for the UV excitation case exhibited similar double exponential decay compared to the EUV excitation case, regardless of the huge difference of the excitation photon energy. The excitonic nature of the emission causes the decay behaviour to be similar, regardless of the optical excitation energy. The measured emission decay is sufficiently short for the characterization of the laser plasma EUV sources with nanoseconds duration.

**3.2** Temperature Dependent Spectral Profiles

The temperature dependent spectral profiles of the ZnO emission are shown in Fig. 3. Their peak positions are 3.22 eV (386 nm), 3.23 eV (384 nm), 3.25 eV (382 nm), 3.26 eV(380 nm), 3.29 eV (378 nm) and 3.32 eV(374 nm) for the ZnO sample temperatures of 298 K, 244 K, 192 K, 138 K, 105 K and 25 K, respectively. Increasing the temperature within this range gradually shifts the emission peak position from 3.32 eV to 3.22 eV. The peak positions and the full width at half maximum (FWHM) of the emission as a function of the temperature is shown in Fig.4. This corresponding shift to lower energy appears to depend linearly on the temperature increase and is also accompanied by a broadening of the spectral width as shown in Fig.4. Increasing the temperature within this range gradually increases the spectral width from 0.05 eV at 25 K to 0.14 eV at 298 K. In general, this emission originates free excitons and bound excitons.[14] The spectral shifts are due to the temperature dependence of the ZnO bandgap and the line width increase is possibly due to thermal broadening effects and to electron-phonon interaction, which causes a broadening of 0.1 eV at a room temperature.[15] Moreover, these spectral properties for the EUV excitation case are almost identical to that of the UV excitation case.

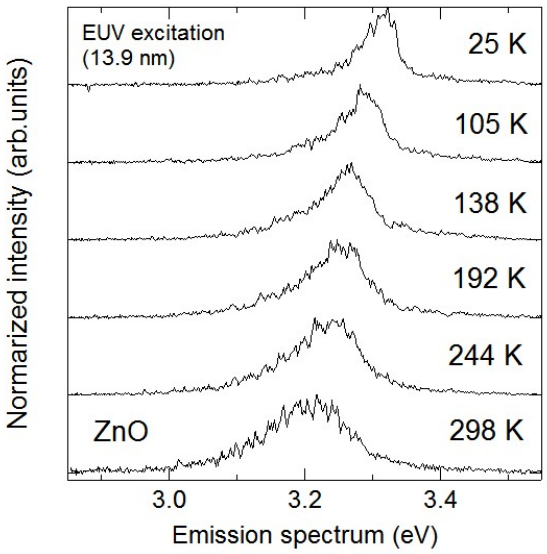


Fig.3 Emission spectra of ZnO, which is excited by EUV laser light (13.9 nm) at the different sample temperatures, namely; 298 K, 244 K, 192 K, 138 K, and 25 K.

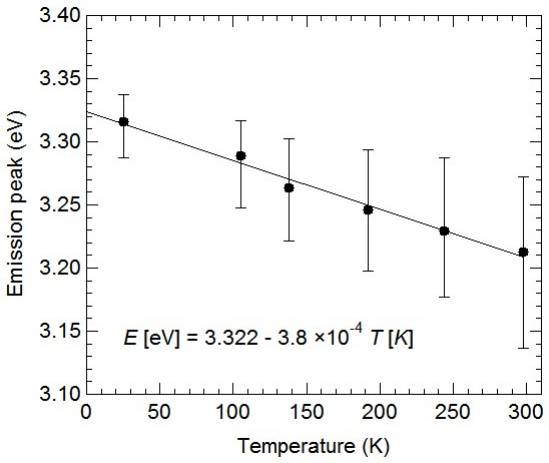


Fig.4 Peak positions of the ZnO emission when the EUV laser pulse irradiates onto the ZnO crystal at the different temperature condition. Bars indicate the spectral width of the emission peaks.

## 4. Summary

In summary, a nickel-like silver laser emitting at 13.9-nm wavelength was used to evaluate the scintillation properties of a hydrothermal method grown zinc oxide (ZnO) crystal in an extreme ultraviolet region. The streak images were used to study the temperature dependence and decay time of the ZnO emission from 25 K to 298 K. Increasing the temperature within this range gradually shifts the emission peak position from 3.32 eV to 3.22 eV. Additionally, its FWHM increases by 0.09 eV from 0.05 eV (at 25 K) to 0.14 eV (at 298 K). Finally, the measured emission decay at 105 K was fitted by a double exponential decay to be $\tau_1$=0.88(4) ns, and $\tau_2$=2.7(2) ns. This decay time of a few nanoseconds is sufficiently short for the characterization of laser plasma EUV sources with nanoseconds duration and is suitable for lithographic applications. The high availability of large-sized ZnO crystals up to 8 cm diameter should make this material attractive for EUV imaging applications.

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## References

1) B. Wu and A. Kumar, J.Vac.Sci.Technol.B **25** (2007) 1743.
2) Y. Shimada, N. Nishimura, M. Nakai, K. Hashimoto, M. Yamaura, Y. Tao, K. Shigemori, T. Kawamura, A. Sunahara, T. Nishikawa, et al. Appl. Phys. Lett. **86** (2005) 51501.
3) S. Fujioka, H. Nishimura, K. Nishihara, A. Sasaki, A. Sunahara, T. Okuno, N. Ueda, T. Ando, Y. Tao, Y. Shimada, et al. Phys. Rev. Lett. **95** (2005) 235004.
4) H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, H. Hosono, Appl. Phys. Lett. **77** (2000) 475.
5) P. Xu, X. Wen, Z. Zheng, G. Cox, H. Zhu, J. Lumin. **16** (2007) 641.
6) M. Ichimiya, T. Horii, T. Hirai, Y. Sawada, M. Minamiguchi, N. Ohno, M. Ashida, T. Itoh, J. Phys.; Condens. Matter **18** (2006) 1967.
7) W. Cao and W. Du, J. Luminescence, **124** (2007) 260.
8) E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, and T. Fukuda, J. Cryst. Growth **260** (2004)166.
9) T. Kawachi, M. Kado, M. Tanaka, A. Sasaki, N. Hasegawa, A. V. Kilpio, S. Namba, K. Nagashima, P. Lu, K. Takahashi, et al. Phys. Rev. A, **66** (2002) 33815.
10) A. Klisnick, J. Kuba, D. Ros, R. Smith, G. Jamelot, C. C. Popovics, R. Keenan, S. J. Topping, C. L. S. Lewis, F. Strati, et al. Phys. Rev. A **65** (2002) 33810.
11) M. Tanaka, M. Nishikino, H. Yamatani, K. Nagashima, T. Kimura, Y. Furukawa, H. Murakami, S. Saito, N. Sarukura, H. Nishimura, et al. Appl. Phys. Lett. **91** (2007) 231117.
12) M. Tanaka, M. Nishikino, T. Kawachi, N. Hasegawa, M. Kado, M. Kishimoto, K. Nagashima, Y. Kato, Opt. Lett. **28** (2003) 1680.
13) J. Wilkinson, K. B. Ucer, R. T. Williams, Radiat. Meas. **38** (2004) 501.
14) Y. Chen, D. Bagnall, T. Yao, Mater. Sci. Eng. B **75** (2000) 190.
15) R. Hauschild, H. Priller, M. Decker, J. Brücker, H. Kalt, and C. Kilingshirn, Phys. Stat. Sol. **3** (2006) 976.