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論文内容の要旨

Owing to the recent progress in laser technology, highly intense extreme ultraviolet (EUV) sources based on laser-produced plasma have been receiving strong interest for various applications, such as the processing technique of next generation semiconductor based on EUV lithography, and spatially and temporally highly resolved imaging of living cells. Due to the variation of the applications, improvement of EUV sources to suit each use has been intensively studied. Among these laser plasma EUV sources, an x-ray laser is a characteristic source with short pulse duration of several pico-seconds, narrow spectral width of less than 10^{-4} for $\Delta\lambda/\lambda$, and possibility of high coherence. The high spatial coherence is especially an important factor because the x-ray beam can be focused to a spot diameter of the wavelength order if the focusing system has sufficient precision. With pulse duration of several pico-seconds, the small focal-size realizes the imaging of high-speed phenomenon in the micro domain. Furthermore, x-ray lasers are expected as a source of interference measurements for evaluating EUV optical system and surface accuracy of optics in the field of EUV lithography. For the present measurement, synchrotron radiation is used by inserting a monochromator and pinholes in the undulator line. This can also be done in a laboratory scale by using an x-ray laser as EUV source.

At the Advanced Photon Research Center, the x-ray lasers generated with transient gain collisional excitation (TCE) method have been studied and have achieved the saturation amplification of a nickel-like silver x-ray laser at the wavelength of 13.9 nm. The TCE scheme have several advantages, such as short pulse duration less than ten pico-seconds, and a high gain generation with low excitation energy of several tens of Joules. In particular, EUV with the wavelength of around 13 nm is useful for lithography, imaging, and interference measurement because the multilayer mirror with high reflectance is commercially prepared. However, the beam divergence of the x-ray laser generated with TCE method is as large as 10 mrad and spatial coherence is not sufficient. In this study, the beam divergence and spatial coherence of the TCE x-ray laser was improved and applied to measurement of time resolved emission spectroscopy.

As an application of the x-ray laser, the scintillation properties of a zinc oxide (ZnO) single crystal are evaluated for EUV using a 13.9 nm x-ray laser. For next-generation lithography applications, various efforts have been made not only for demonstration of efficient EUV sources, but also for the development of functional optical components in the EUV region. In particular, the development of efficient and fast imaging scintillator devices with sufficient size is a key element for lithographic applications. In these aspects, hydrothermal method grown ZnO is a prominent candidate. Currently, its growth characteristics have been greatly improved in the aspect of crystalline quality and size of up to 3-inch-diameter. ZnO has been intensively studied for the past ten years as a light-emitting diode material and as a nano-structured material to improve the optical properties including response time. The advantage of bulk ZnO is the availability of large sized homogeneous crystal with a reasonable fabrication cost. For the evaluation of hydrothermal method grown ZnO, a nickel-like silver x-ray laser operating at 13.9 nm is the ideal light source; having large pulse energy up to about micro-joules level and a sufficiently short pulse duration down to several picoseconds.

The improvement of the nickel-like silver x-ray laser at the wavelength of 13.9 nm is described in chapter 2. To decrease the beam divergence of the x-ray laser, we have used the double target configuration. On this technique, a part of the x-ray laser generated in the first medium is used as the seed x-ray laser, and it is injected into the successive second medium, which is used as an amplifier with calm density gradient. The gain medium plasmas are generated with a chirped pulse amplification Nd:glass laser system with two beam lines. Each beam consisted of two pulses; a pre-pulse with a pulse duration of 300 ps and a picosecond heating pulse with a temporal delay of 600 ps from the pre-pulse. The pulse duration of the heating pulse for the first target is 4 ps with the quasi-travelling wave arrangement and that for the second target is 12 ps without the travelling wave. The total pumping energy is set to be 14 J for the first target and 11 J for the second target. The energy ratio of the pre-pulse and the heating pulse is 1:8. The laser pulses are focused with a line shape of 6.5 mm × 20 μm on flat silver targets with an irradiance of the heating pulse of $\sim 10^{15}$ W/cm^2. The distance between the two targets is 20 cm. The far field patterns of the x-ray laser are measured for several seed timing by changing the optical delay of the pumping laser of the first target. At the timing of -15 ps, only the seed x-ray laser from the first target is observed. The beam divergence of the seed x-ray laser is approximately 6 mrad in full width at half maximum (FWHM). The total energy of the seed x-ray laser is 270 nJ. For the seed timing of 0 ps and +15 ps, the intense beams amplified in the second medium was observed. When the timing is adjusted to be 0 ps, an intense x-ray laser beam with little divergence of 0.5 mrad in direction parallel to the target surface is observed outside the shadow of the second plasma. The beam is spread in the direction perpendicular for 2.5 mrad. This means that the seed x-ray is amplified in the high gain region, where the refraction is dominant. Delaying the pumping time of the seed x-ray from the timing of 0 ps, the spreading x-ray laser becomes weaker, and an intense and narrow spot appears inside the shadow of the plasma. At the timing of +15 ps, only the narrow spot is observed, which can be fit well with a Gaussian profile. The beam divergence is obtained to be a much-reduced value of 0.20 mrad (FWHM) for the directions perpendicular and parallel to the target surface. The diffraction limited beam divergence for a coherent Gaussian beam with a source size of 50 μm is analytically calculated to be 0.11 mrad. The observed divergence is only 1.8 times greater than this value. This implies that the obtained x-ray beam is quite close to the diffraction-limited condition. The gain coefficient of the amplifier plasma at the timing of +15 ps is estimated to be 7.9 cm^{-1} with exponential fitting to the data. This value is smaller than the gain coefficient of the single target, which is observed to be 35 cm^{-1} in a previous study. This small gain coefficient and small beam divergence suggest that the gain region of this highly directed beam is located in a low density area, where the influence of refraction is negligible.

In order to characterize the spatial coherence of the x-ray laser beam, we carried out a Young's double slit experiment. A pair of slits with width of 16 μm and separation of 150-350 μm is placed 2.3 m away from the second target where the beam diameter is 460 μm. Even the 350 μm separated double slit, the interference pattern with high contrast was observed for both parallel and perpendicular direction. Assuming the Gaussian shell model for the x-ray laser source, the spatial coherence length can be determined by the visibility of the fringe patterns. For both the parallel and perpendicular direction, the spatial coherent length is estimated to be about 600 μm, which is longer than the beam diameter at the position of the double slit. It means that this narrow beam is spatially fully coherent.

The evaluation of the scintillation properties of ZnO single crystal for EUV lithography is described in chapter 3. The x-ray laser operated at 13.9 nm was employed as the excitation source. The lasing scheme is the 4p-4d transition of the nickel-like silver ion pumped with TCE method. The typical pulse energy of the x-ray laser emission was 0.5 μJ and the duration was 7 ps. This value is sufficiently short for this experiment. The single crystal ZnO sample is grown by hydrothermal method combined with a platinum inner container. High-purity and transparent ZnO single crystal with a large size of 50 × 50 × 15 mm^3 was sliced with a (0001) surface orientation. The x-ray laser was focused on the sample using a molybdenum/silicon multilayer spherical mirror suitable for 13.9 nm. In spite of the huge photon energy compared with the bandgap, no visible color center was observed after about 50 shots irradiation. To eliminate continuous emission from the plasma, a 0.2 μm-thick zirconium foil was placed before the EUV mirror. The fluorescence spectrum and the fluorescence lifetime of the ZnO sample were measured using the 25 cm-focal-length spectrograph coupled with a streak camera with the temporal resolution of 100 ps in the fastest scanning range. The trigger pulse of the streak camera was provided by a pulse generator, which also served as the master clock of the x-ray laser. For comparison, the scintillation properties were also evaluated using the 351 nm third harmonics from the 1053 nm chirped pumping source for the x-ray laser. The ZnO was excited at energy slightly above the bandgap. The pulse duration of the 351 nm excitation is measured to be 110 ps.

One shot of x-ray laser was enough to obtain an image of the time-resolved fluorescence spectrum. To reduce the noise level, three frames were integrated to obtain a clear streak image. The time profile at the peak of the spectrum can be expressed by a double exponential decay with time constants of 1 ns and 3 ns. The two decay constants have been measured in several works for UV excited ZnO single crystals. The fast decay is the lifetime of free exciton and the slower decay is assigned to be trapped carriers. The corresponding fluorescence spectrum and the time profile of UV excitation is also measured. In both the excitation conditions, a prominent fluorescence peak of the ZnO exciton transition was observed at around 380 nm. This wavelength is still convenient for high resolution imaging devices, since even BK7 glass is transparent at this wavelength. Moreover, the two decay lifetimes observed in both cases were almost similar regardless of the huge difference in the excitation photon energy. The fluorescence lifetime is sufficiently short for the characterization of the laser plasma EUV source with nanoseconds duration for lithographic applications. Furthermore, a large-sized and homogeneous material is potentially attractive for EUV imaging applications including lithography.

論文の審査結果の要旨

本論文は、レーザー生成プラズマをベースとする高輝度パルスＥＵＶ光源であるＸ線レーザーのビーム発散角の改善と、これを用いた固体の時間分解分光の研究成果についてまとめたものである。論文は日本語で書かれており、４章で構成されている。第１章の序論にはＸ線レーザーの背景と研究の意義と目的、第２章にはＸ線レーザーの発生原理、発振の実際と空間コヒーレンスを含むビーム評価について、第３章にはＸ線レーザーを励起光源とした酸化亜鉛単結晶を中心とした固体の時間分解分光計測について、第４章に全体のまとめが記述されている。

Ｘ線レーザーは、数ピコ秒のパルス幅、狭い波長幅、そして原理的に高い空間コヒーレンスを持ち得るといった性質を持った特徴的な光源である。特に、波長 13~14nm 付近では高い反射率の多層膜光学素子が作成可能であるため、ＥＵＶリソグラフィーに用いられる光学系の評価等への様々な応用が期待されている。一方、本研究で用いたＸ線レーザーは当初ビーム発散角が 10 mrad 程度と大きく、利用実験に供するには空間的制約が大きかった。本研究では、距離を離して並べた２つのＸ線レーザー媒質を用い、第１の媒質で発振したＸ線レーザー光のうち、空間コヒーレンスの高い成分のみを第 2 の媒質で増幅すると共に、第 2 の媒質を励起するタイミングを制御することにより、媒質の密度勾配による屈折の影響で媒質内を伝播中のＸ線レーザーが広がる効果を低減した。この結果、波長 13.9 nm で発散角が 0.2 mrad というほぼ回折限界の発振に成功し、簡単な光学系のみでビームラインを構築して利用研究の推進を可能とした。

Ｘ線レーザーを光源として用いた利用研究としては、波長 13.9 nm 励起による酸化亜鉛単結晶のエキシトン発光の時間分解分光計測を行った。その結果、発光寿命がナノ秒程度であり、発光の時間減衰やスペクトルが紫外光による直接励起の場合と変わらないことを見いだした。このことは、シンチレーターとして用いる際に一般的な紫外光源により事前にアライメントが可能であることを意味している。また、数ナノ秒から十数ナノ秒とされるＥＵＶリソグラフィー用光源のパルス幅と比べ十分発光寿命が短いことから、この物質がリソグラフィーをはじめとする波長 13~14nm 領域用のシンチレーターとして好適であることを示している。酸化亜鉛は近年、高品質の大型単結晶の量産化が精力的に研究されており、これをシンチレーターとして用いることで、従来は高額で繊細な扱いを要求される軟Ｘ線検出器に頼っていたＥＵＶ観測を、安価で容易にすることが期待されるため、この可能性を実証した本研究の意義は高い。また、波長 13nm 領域の励起でシングルショットの時間分解発光計測に成功した例は他になく、本研究はＸ線レーザーがＥＵＶ領域の発光計測や光学素子評価に有用なツールであることを示しただけではなく、今後、高輝度な光源が存在しないために詳細な研究が成されていなかった固体のＥＵＶ、ＶＵＶ領域での発光分光研究に新たな展開を与えたという点においても評価は高い。以上の点を考慮し、審査委員会全員一致で本申請論文は博士（工学）の学位論文として十分であると判断した。