Spectroscopy for identification of plasma sources for lithography and water window imaging

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Abstract. The identification of sources for applications that include nanolithography, surface patterning and high resolution imaging is the focus of a considerable activity in the extreme ultraviolet (EUV) or soft x-ray (SXR) spectral regions. We report on the result of a study of the spectra from laser produced plasmas of a number of medium and high Z metals undertaken in order to identify potential sources for use with available multilayer mirrors. The main focus was the study of unresolved transition arrays emitted from ions with 3d, 4d and 4f valence subshells that emit strongly in the water window (2.34-4.38 nm).and that could be used for biological imaging or cell tomography.

1. Introduction:
EUV lithography at 13.5 nm is currently being introduced into high volume manufacturing for the production of integrated electronic circuit components with typical dimensions of 22 nm or less. The choice of this wavelength is based on the availability of Mo/Si multilayer mirrors (MLMs) with a reflectivity of ~70% at this wavelength and the optimum source has been identified as Sn, as lines from transitions of the type 4p6d⁰ -4p6d⁰⁰⁰ + 4p⁰⁶d⁰⁰⁰⁰⁰⁰⁰⁰ f overlap in Sn¹⁰⁺ to Sn¹³⁺ at this wavelength [1]. The conversion efficiency (CE) of laser to EUV energy in a 2% bandwidth at 13.5 nm, corresponding to the reflectance bandwidth after eleven reflections in commercially available sources is now in excess of 4%. The theoretical maximum is significantly greater and recent experiments point towards a CE of ~7% being attainable [2].

Recently the development of LaB⁶/C MLMs, with theoretical reflectance approaching 80% at around 6.7 nmhas led to proposals to introduce a future generation of lithography at this wavelength for the manufacture of circuits with even smaller feature sizes. The optimum sources were identified as laser produced plasmas of Gd and Tb, as a large number of Δn= 0,
n=4-n=4 transitions in their ions emit strongly near this wavelength. Because of their complexity these transitions give rise to an unresolved transition array (UTA) [3]. However to date, the highest CE obtained, for laser to EUV energy emitted within the 0.6% wavelength bandwidth of the mirror is only 0.8%, pointing to the need to identify other potential sources or selection of other wavelengths [4].

Sources for other applications are also being developed. Conventional sources for soft x-ray microscopy in the water window spectral region where carbon absorbs strongly but oxygen is essentially transparent, i.e. from 2.34-4.38 nm, use H-like line emission from liquid nitrogen or carbon containing liquid jets which can be focused using zone plates [5]. Recently the possibility of using MLMs with n=4-n=4 emission from a highly charged Bi plasma was proposed [6] and subsequently the possibility of using Δn=1 transitions in 3rd row transition elements was identified [7]. Both of these proposals rely on the existence of spectral features that coincide with the reflectance characteristics of available MLMs, shown in the table below [8].

| MLM       | Wavelength (nm) | Reflectivity (%) |
|-----------|-----------------|------------------|
| Cr/V      | 2.42            | 9                |
| Cr/Ti     | 2.73            | 17               |
| TiO$_2$/ZnO | 2.74         | 29               |
| Cr/Sc     | 3.14            | 21               |
| Cr/Sc B$_4$C | 3.15        | 32.1             |
| Cr/Sc     | 3.35            | 10               |

In order to identify suitable transitions that could be used with these MLMs for water window imaging, we have systematically studied the emission from laser produced plasmas of a large range of elements from Z=39 (Y) to Z=84 (Pb).

2. Experimental details:

In the majority of experiments, planar targets were irradiated in vacuum (10$^{-6}$ mbar) by two table-top Nd:YAG laser systems operating at $\lambda$=1064 nm producing power densities ranging from $3.0 \times 10^{13}$ W/cm$^2$ to $2.6 \times 10^{14}$ W/cm$^2$ at a pulse duration of 150 ps (FWHM) and $1.3 \times 10^{12}$ W/cm$^2$ to $5.5 \times 10^{12}$ W/cm$^2$ for a pulse duration of 10 ns (FWHM), respectively. Both lasers were operated in single shot mode. A flat field grazing incidence spectrometer with a 2400-grooves mm$^{-1}$ variable line space grating was used to disperse the XUV radiation in the 1-7 nm range, while a 1,200-grooves mm$^{-1}$ variable line space grating was used to extend the coverage to longer wavelengths. Time-integrated spectra were recorded using a thermoelectrically cooled back-illuminated X-ray charge coupled device (CCD) camera and the spectra were corrected for the CCD response which, unlike the grating response, was measured for this wavelength region. The typical instrumental spectral resolution was ~0.01 nm and the calibration uncertainty was within ±0.009 nm throughout the spectral range investigated. The critical electron density corresponding to that at which most of the laser energy is absorbed is ~$10^{21}$ cm$^{-3}$ meaning that the ion density in the hot, EUV emitting region lies in the range $10^{18}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$. As a result, Nd:YAG laser produced plasmas (LPPs) using pure metallic targets produce spectra that are optically thick to the strongest resonance lines [9]. Since the plasma emission is integrated over the entire plasma lifetime, it contains emission from many ion stages simultaneously, so in order to get ion stage specific information, the LPP spectra were supplemented by spectra from low density, optically thin plasmas recorded at the Large Helical Device at the National Institute for Fusion Science at Toki and ion stage differentiated spectra at the compact electron beam ion trap (CoBIT) at the University for Electro-communications in Tokyo.
3. Results:
The emission spectra are in every case dominated by unresolved transition arrays or UTAs. Two types of UTA occur $\Delta n=0$ and $\Delta n=1$. In the $\Delta n=0$, $n=4 - n=4$ arrays, transitions in adjacent ion stages tend to overlap and whose positions shift to shorter wavelength with increasing atomic number as shown in Figure 1 [10]. In addition, a small number of intense emission lines from closed shell (Pd-like, 4d$^{10}$) and single electron (Ag-like, 4d$^{10}$4f, and Rh-like, 4d$^3$) species are generally superimposed on the UTA. Because of their intensity these UTAs are already used as sources for lithography at 13.5 nm and have been suggested as sources for 6.7 nm nanolithography [11]. In these applications, high conversion efficiency (CE) is required and using slab targets with Nd:YAG lasers, CEs of around 2.3% and 0.3% have been obtained within the reflectance bandwidths of the appropriate mirrors [9,12]. Since both MLM bandwidth and UTA emission efficiency decreases with decreasing wavelength, CEs in the water window are expected to be significantly lower. However since such sources are being developed for imaging rather than high volume manufacturing, CE is not as pressing an issue. For these arrays the emission of Au, Pb, and Bi lie in the water window region and have peaks centred near 4.1 and 4.0 nm, respectively [13], though their intensity is relatively weak as emission from high ion stages necessitates electron temperatures in excess of 500 eV [6]. For example, the strongest discrete line expected, the 4d$^{10}$-4d$^9$4f$^1$P$^1$-S$^0$ appears at 3.987 nm in Pb$^{36+}$ and 3.8966 nm in Bi$^{37+}$ [13].

In contrast, $\Delta n=1$ UTAs are usually observed at a lower plasma electron temperature. We have systematically investigated the emission from 3d-4p and 4f arrays in the 2nd transition row elements from Y (Z=39) through Pd (Z=46) and 4d-5p, 4d-5f and 4f-5g arrays in a number of the elements from Hf (Z=72) through Bi (Z=83). The spectrum obtained for Mo (Z=42) is shown in figure 2. Note that this spectrum was previously analysed by Schweitzer et al. [14]. It is seen from this figure that there is a good match between the observed UTA peaks and two of the most promising MLMs with optimum reflectance at 2.74 and 3.15 nm, so that Mo$^{18+}$ (3d-4f) and Mo$^{20+}$ (3d-4p) are potentially suitable sources for water window imaging using reflecting optics [15]. Note also that the plasma temperatures required are much lower than those required for the $n=4 - n=4$ UTA in Pb or Bi. The variation of ionic populations with electron temperature calculated using the collisional radiative equilibrium (CRE) model of Colombant and Tonon [16] is shown in figure 3. In performing the calculation, it was assumed that the electron density corresponded to the cutoff density for Nd:YAG radiation i.e. $10^{21}$ cm$^{-3}$. From this figure it is seen that the populations of Mo$^{18+}$ and Mo$^{20+}$ are
maximised close to plasma electron temperatures of 140 and 180 eV, respectively. For other elements, the UTAs were identified either from previous work [15 and references therein] or from Hartree-Fock with configuration interaction (HFCI) calculations performed with the Cowan code [17]. In figure 4, the observed positions of the UTA peaks for Y, Nb, Mo, Ru, Rh and Pd and their calculated widths as determined within the UTA formalism [3] are shown. It is clear that the UTAs for a particular transition type move systematically to shorter wavelength with increasing ionic charge and increasing electron temperatures.

Fig.2. Emission from LPPs produced by Nd:YAG lasers with different pulse durations. The position of the mean wavelength for each array is also indicated.

Fig.3. Ion fractions of Mo LPPs as a function of electron temperature, an electron density of $10^{21}$ cm$^{-3}$ is assumed. The electron temperatures corresponding to three different laser power densities, $3 \times 10^{10}$ W cm$^{-2}$, $3 \times 10^{11}$ W cm$^{-2}$ and $2.2 \times 10^{12}$ W cm$^{-2}$ are shown.
atomic number. As a consequence, opacity effects, which greatly limit the intensity available from \( \Delta n=0 \) arrays, since emission from more highly charged ions is reabsorbed by overlapping transitions in ions of lower charge states, are less important for \( \Delta n=1 \) transitions.

It is also known that 4f\(-5g\) transitions in 3\(^{rd}\) transition row elements also lie in the water window region [18]. We have also obtained and identified structure resulting from these and 4d\(-5p\) and 4d\(-5f\) arrays. These arrays merge to form a broad quasicontinuum feature with the individual UTAs providing a series of minor peaks superimposed on it [19]. An example, showing the spectrum of Re\((Z=75)\) obtained with both ps and ns LPPs is presented in figure 5 where the UTA peaks, labelled from A to Z7 are clearly seen in the ps spectrum. From this figure two features are immediately
obvious. First, the 4f-5g transitions contribute at lower energy followed by the 4d-5p and 4d-5f arrays as the photon energy increases. Note that the 4f-5d transitions are found at longer wavelength and do not contribute to the spectrum shown here. Secondly, the emission from the ps plasma extends much further to shorter wavelength reflecting the fact that more highly ionised stages, with open 4d valence subshells are produced in the ps LPPs because of the higher plasma temperatures produced by the higher flux density which is almost two orders of magnitude greater than in the case of the ns plasma. Around Z=75, the contribution from the 4d-5p and 4d-5f transitions is strong especially in ps LPPs and dominate the higher energy end of the observed emission where they give rise to the peaks labelled from A to I and J to S, respectively. With increasing atomic number, as expected, their contribution relative to the 4f-5g UTAs, which shift to shorter wavelength, decreases so that by Pt (Z=78), the water window spectrum is largely dominated by 4f-5g arrays. In addition there is also a strong contribution from 4f-5g satellite transitions of the form \(4f_{N-1}^N 5s-4f_{N-2}^N 5s5g\), which are comparable in intensity to the \(4f^N 4f^{N-1} 5g\) resonance array [19]. Note that virtually all of the elements from Hf to Pb, contain features that match with some available MLMs.

Fig.5. Comparison of emission from LPPs produced by 170 ps and 7 ns Nd:YAG pulses. The emission from the former contains a greater contribution from higher ion stages. The spectral regions where 4d-5f, 4d-5p and 4f-5g transitions contribute are shown.

Currently we are characterising these transitions in other elements along this sequence. We are also in the process of calibrating the spectrometer response to test the viability of determining ion populations from the observed emission in order to benchmark and refine the plasma codes used to describe LPPs. This is particularly necessary to characterise picosecond plasmas where equilibrium is generally not established during the pulse illumination time.

4. Conclusions:
We have found that a number of transition arrays can be found to match the reflectance characteristics of MLMs in the EUV and SXR spectral regions. We intend to extend the study of 4d-ni and 4f-5g arrays to the lanthanides, to explore how 4f level crossing effects complicate the spectra and also to complete our investigation and identification of these transitions in other high Z elements.
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