Optical emission spectroscopy of plasma produced by laser ablation of iron sulfide

S Karatodorov[1,3], V Mihailov[1], T Křenek[2] and M Grozeva[1]

[1]Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences,
 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[2]Research Center of New Technologies, University of West Bohemia,
 30614 Plzeň, Czech Republic

E-mail: skarat@issp.bas.bg

Abstract. Optical emission spectroscopy studies are reported of laser ablation plasma from an iron sulphide (FeS) target in vacuum. The plasma emission is characterized with spatial and tempoal resolution. The spectral observations are used to calculate the electron plasma parameters. The electron temperature is calculated by the Boltzmann plot method and the electron number density, by the Stark broadening of the emission lines.

1. Introduction

One of the key applications of laser ablation is pulsed laser deposition. The pulsed laser deposition (PLD) is a widespread technique for preparing micro- and nano-structures, e.g. thin films, nano-particles, etc. One of the key advantages of this technique is the possibility to evaporate various kind of materials, i.e. solid, liquid, non-conductive [1], and to transfer the stoichiometry of the target materials to the deposit on the substrate [2]. Recently, interest has been shown in pulsed laser deposition of iron sulfide (FeS) thin films [3]. The FeS semiconducting and magnetic properties and the abundance of a low-price non-toxic raw material [4], make FeS thin films produced by pulsed laser deposition very attractive for solar cell fabrication.

Under PLD conditions, the laser-generated plasma is the carrier of evaporated material from the target onto the substrate surface. Thus, the deposition results depend on the plasma dynamics. This stresses the importance of investigating the plasma parameters and their evolution in time and space. The plasma parameters can be correlated to the thin-film structure deposited. This would give one the opportunity to tune the resulting deposition by tuning the plasma parameters. Thus, knowledge of the plasma evolution would enable one to control the deposits produced.

This work was aimed at obtaining the plasma parameters under conditions similar to those for actual pulsed laser deposition of iron sulfide. The laser ablation was investigated of an iron sulfide (FeS) target in vacuum by a pulsed 1064 nm Nd:YAG. The plasma evolution was studied by optical emission spectroscopy with spatial and temporal resolution. The electron temperature and number density were extracted from the time-resolved spectral observations. The electron temperature was calculated by the Boltzmann plot method and the electron number density was evaluated by the Stark broadening of the excited emission lines.

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[3] To whom any correspondence should be addressed.

2. Experimental setup and conditions

The experimental setup for plasma emission investigation of laser ablation from an iron sulphide target consists of three parts – an excitation laser with delivery optics, a vacuum chamber with the target and a spectroscopic registration system. The setup is shown schematically in figure 1.

The laser is a pulsed Nd:YAG Quanta Ray GCR 3 emitting at the fundamental wavelength of 1064 nm. The pulse energy is fixed at 20 mJ and the pulse duration is 8 ns. The laser is directed to the target by a dielectric mirror at 45 degrees. The laser beam is focused on the target by a glass lens with a 25-cm focal distance.

The FeS pellet target is situated in a rectangular metal vacuum chamber. The chamber has quartz windows on three of the sides enabling laser excitation and spectra collection from orthogonal directions. The vacuum chamber is evacuated by an AV 63 Lavat a.s. diffusion vacuum pump ($< 10^{-6}$ Torr).

The registration system consists of a Mechelle 5000 monochromator with Andor iStar DH734-18F-03 ICCD camera and optical fiber (50 μm). The Mechelle 5000 system has the advantage of recording the whole spectral range 240÷800 nm in one camera shot.

In performing each measurement, the iron sulfide pellet was placed in the vacuum chamber. The chamber was evacuated to $< 10^{-5}$ Torr. The optical fiber was placed parallel to the target surface at around 1 mm (close to the ablation volume) or 3 mm above it. The chosen laser pulse-registration delay was set in the range 20÷1000 ns. The laser pulse was fired to generate the plasma from the target material. The laser pulse triggered the optical diode and the registration system. The spectrum was recorded at the set delay time with a camera gate of 40 ns.
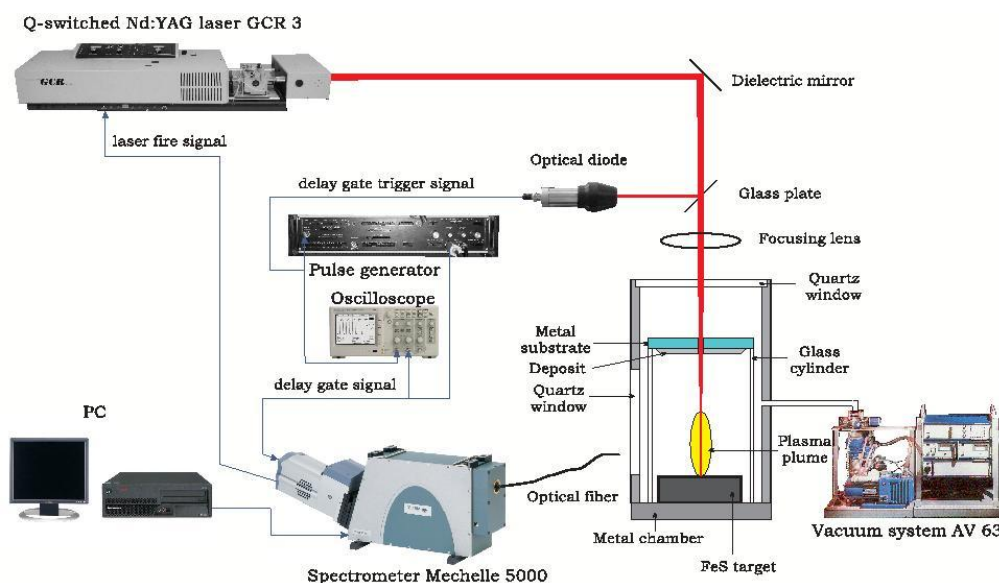

Figure 1. Experimental setup.

3. Experimental results

The laser-induced plasma exhibits a fast expansion in vacuum. It has a weaker spectral emission compared to the emission at higher pressures because of the predominant dissipation of the absorbed laser energy in the directed kinetic motion of the plasma species [5, 6].

Typical emission spectra obtained for 1-mm distance and time-delays between 20÷600 ns are presented in figure 2. The spectra shown are limited to the wavelength region 400÷425 nm. As can be seen, there is a decay of the plasma emission with a lifetime of around 500 ns. These characteristics are valid for the full wavelength interval 240÷800 nm recorded in the experiments.

The plasma emission spectra recorded contain a large number of Fe lines and almost completely lack sulfur lines. This is due to the fact that the strong emission lines of neutral sulfur are in the UV and near IR and only weak singly ionized lines are present in the visible region ([7] and references therein). This fact limited the investigation presented here to using only Fe lines for the calculation of the plasma parameters.
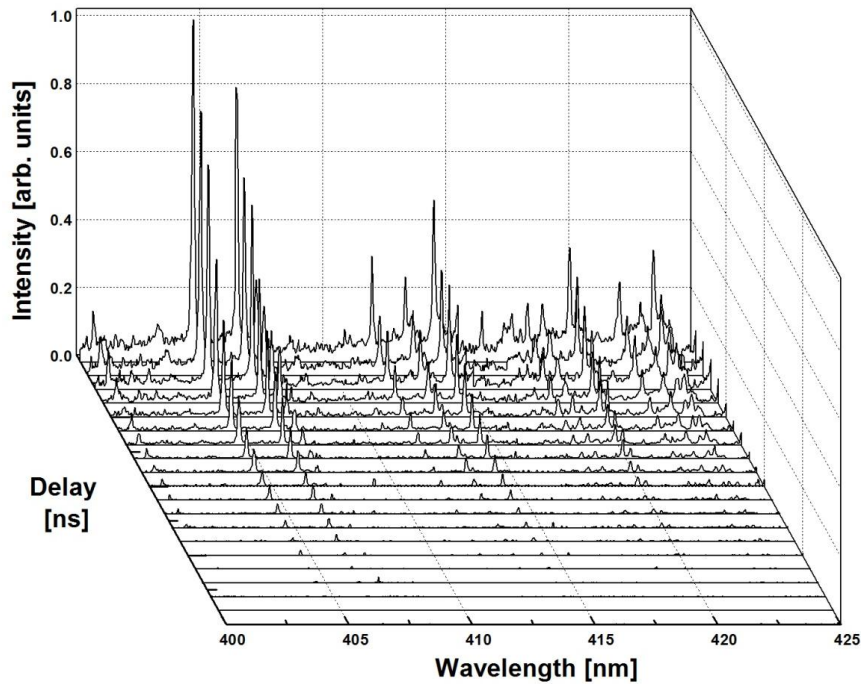
Figure 2. Emission spectra obtained from a FeS sample for 1-mm distance and time delays between 20÷600 ns.

3.1. Electron temperature

The electron temperature is an essential plasma parameter. In the presence of a local thermodynamic equilibrium (LTE), the electron temperature governs the excited levels distribution as described by the Boltzmann equation. In order for the LTE to be satisfied, the electron number density should be high enough so that the excitation rates are higher than the radiative rates. Under these conditions, the excitation electron temperature from the Boltzmann equation coincides with the electronic temperature from the Maxwellian velocity distribution.

The most widely used way of obtaining the electron temperature of laser-induced plasma is the Boltzmann plot method, which is applicable when the local thermodynamic equilibrium is satisfied. The method calculates the electron excitation temperature by measuring the lines intensities from single species. If multiple lines are included, then the good correlation of the experimental data to its linear fit is a reasonable validation of the use of the Boltzmann plot method.

The simplest form of the electron excitation temperature dependence on the species line intensities [8] is given by:

$$\ln \frac{I\lambda}{Ag} = -\frac{E}{kT},$$

where I is the measured line intensity, λ is the line wavelength, A is the transition probability, g is the upper level degeneracy, E is the upper level energy, k is the Boltzmann constant and T is the electron excitation temperature.

A set of 14 Fe I emission lines was used to construct the Boltzmann plot. The lines characteristics are shown in table 1. The set of lines was adapted from [8].

Table 1. Wavelength, upper-level energy, lower-level energy, upper-level degeneracy and transition probability of the Fe I lines used for the Boltzmann plot.

| Fe I lines parameters				
Wavelength [nm]	E_j [eV]	E_i [eV]	g_j	A_{ij} [$10^8 s^{-1}$]
368.22	6.91	3.55	5	1.7
368.41	6.09	2.73	7	0.34
368.74	4.22	0.86	9	0.0801
370.56	3.4	0.052	7	0.0322
370.92	4.26	0.91	7	0.156
372.76	4.28	0.96	5	0.225
373.24	5.52	2.2	5	0.28
382.78	4.8	1.56	5	1.05
385.64	3.27	0.051	5	0.0464
386.55	4.22	1.01	3	0.155
387.25	4.19	0.99	5	0.105
389.57	3.29	0.11	1	0.094
389.97	3.27	0.087	5	0.0258
390.29	4.73	1.56	7	0.214

Figure 3 shows the Boltzmann plot obtained for the lines in Table 1 for a delay of 40 ns and a distance of 1 mm. From the plot, the electron excitation temperature is calculated. It is seen in the figure that the linear fit lies well within the error margins of the experimental data, which justifies the assumption of LTE. The value obtained for the excitation electron temperature is 9800 K (0.84 eV).

3.2. Electron number density
The high concentration of electrons and ions in the laser-induced plasmas make them appropriate sources for the measurement of Stark broadening of the emission lines. The classical Stark broadening theory [9] states that isolated lines of neutral elements, with the exception of hydrogen, are primarily broadened by electrons. The
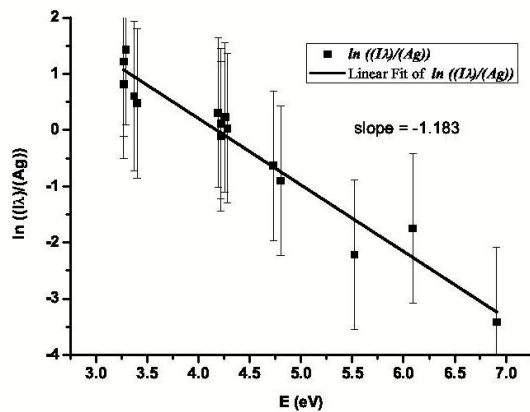
Figure 3. Boltzmann plot of the chosen set of 15 Fe I emission lines.
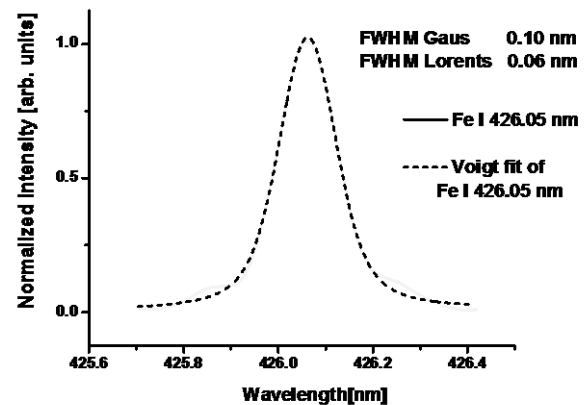
Figure 4. Voigt fit of the Fe I 426.05 nm line.

collision with electron produces a broadened Lorentzian profile of the emission line.

For calculation of the electron number density, the dependence of the Stark broadening on the electron number density is used:

$$\Delta\lambda_{1/2} = 2w \frac{N_e}{10^{16}},$$

where $\Delta\lambda_{1/2}$ is the measured FWHM Lorentzian profile broadening, w is the natural width of the line and N_e is the electron number density.

In order to obtain the Lorentzian broadening profile, the experimentally observed line Fe I 426.05 nm was deconvoluted. For the deconvolution, the apparatus function of the spectrometer was determined by measuring the linewidth of the Nd:YAG laser second harmonic line (532 nm). In figure 4, the Fe I 426.05 nm spectral line is fitted with a Voigt profile having a Gauss component of 0.10 nm and a Lorentzian component of 0.06 nm. The Lorentzian profile FWHM obtained in this way was

inserted in the Stark broadening formula. The data for the *w* Stark parameter of the Fe I line 426.05 nm (0.11 Å) was taken from [10]. The electron number density was calculated to be 2.7×10^{16} cm^{-3} at 60 ns after the laser pulse and was decreasing by one order of magnitude in the next 200 ns.

4. Conclusions

The laser-induced plasma emission from iron sulfide target in vacuum was investigated with spatial and temporal resolution. The electron plasma parameters were calculated from the plasma emission spectra obtained. The Boltzmann plot of the line emission intensities showed an electron excitation temperature of 0.84 eV in the first few tenths of ns after the ablation pulse. For the same time window, the Stark broadening of the Fe I emission line indicated an electron number density of 2.7×10^{16} cm^{-3} with a fast decay in the next 200 ns.

In a future work, the plasma parameters measured here will be used to obtain a correlation with the actual structure of the deposited FeS thin films.

Acknowledgments

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