Spectroscopic diagnostic and structural characterization for (Selenium, Zinc oxide and Manganese oxide) prepared by laser induce plasma

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ABSTRACT. In this paper, the plasma parameters of the three materials (selenium, zinc oxide, and manganese oxide) were calculated using laser induced breakdown spectroscopy, where the plasma is generated by this technique through the interaction of the laser with the solid target and the calculation of the electron temperature and electron density. Also, the structural properties of the prepared thin films were studied. It was found from the standards that the crystal size (XRD) of the three materials decreases with increasing energy, and this corresponds to measurements of (AFM) where the average diameter decreases with increasing energy.

1- Introduction

Due to its versatile and complex nature, laser-induced plasma (LIP) formation is a rapid process which has been under investigation for several decades. For a very short period of time, the intense laser pulse delivers energy to the target surface, which excites, ionizes and vaporizes the material immediately into an extremely hot vapor plume, also known as a 'plasma plume'[1]. LIBS is an atomic emission spectroscopy technique that causes optical sample excitation using highly energetic laser pulses [2]. The interaction between focused laser pulses and the sample produces plasma made of ionized matter. 'Spectral signatures' of chemical composition of many different material types in solid, liquid or gas state [3,4] may be supplied with plasma light emissions. The ablation process is divided into three stages using lasers with long pulse durations (> 1 ns). In the first stage, the laser light interacts with the solid, resulting in quick ionization of the target surface into plasma on a short time scale relative to the duration of the pulse. The laser light is absorbed effectively by the plasma that isothermally expands in the second phase. The resulting plasma plume expands quasi-adiabatically in the third stage after the end of the laser pulse, in a medium that can include vacuum or a background gas [5]. In the emission spectrum, visible lines that are useful for plasma parameters such as electron temperature, electron number density, debye length and plasma frequency estimation are shown. If the plasma is in local thermodynamic equilibrium (LTE), by calculating the electron temperature, the relative strength of two lines originating from the same species form and the same ionization phase can be achieved [6]. In LTE, The plasma temperature is calculated from the equation [7]:

\[ T_e = \frac{h \nu}{k_B} \left( \frac{N_2}{N_1} \right) \]
The number of free electrons per unit volume describes the electron density (ne). For determining electron density, there are several credible methods used, including plasma spectroscopy, microwave and laser interferometry, and Thomson scattering. Electron density determination by linear Stark expansion of plasma spectral lines results from the resulting collisions in line expansion and peak wavelength shift of charged species.

2. Experimental Setup

Optical atomic emission spectra of zinc, manganese, and selenium plasma were calculated using the laser induced breakdown spectroscopy technique as shown in Fig. 1.

This system consists of a laser device (Nd:YAG) with a wavelength of 1064 nm and a pulse duration of 9 nanoseconds with a repetition frequency of 6 hertz, where it is at an angle of 45 with the solid target and the focal length is 10 cm, so the process of contrasting is easier and faster and focusing the laser on a smaller area where the size of the laser spot is The depth and concentration is small and thus the strong breakdown and production of the plasma are shown in the above figure. The optical emission spectroscopy (OES) method was used to determine electron temperatures, plasma frequency densities as well, mathematically determining the length of Debye and Debye number.

3. RESULTS AND DISCUSSIONS

3.1 Plasma spectrum of (Zinc, Manganese and Selenium).

Laser induced (zinc, selenium and manganese) plasma optical emission spectrum of 300 nm to 900 nm plume in ambient air with laser pulse energies of (650, 750, 850 and 950) mJ. The plasma spectrum consists of a number of neutral lines and the assignment of these lines was done using NIST database. Figures (2,3 and 4) shows the highest intensity lines in the plasma spectrum (Zn, Mn and Se) spectral lines in the air ambient. Transitions are identified using the National Institute of Standards and Technology’s spectral data base (NIST). Increases in plasma height and plasma emission are the result of the increase in target ablation. The
plasma shielding effect is observed at higher laser peak power values, i.e. the plasma becomes opaque to the laser beam that shields the target so that the intensity of the lines drops. Due to the variation in their statistical weight, probability of transition and excited energy level, the peak intensities vary from peak to peak. Which according to Boltzmann, designates the number of excited atoms at this level In addition, it can be noted that the difference in the percentage increase in the intensity of the peaks by increasing the laser energy used is due to the difference in plasma temperature that affects the distribution of excited atoms according to Boltzmann[8]. Figures show the variation of electron temperature (Te) and electron density (ne) with laser energy (a, b and c). The electron temperature and electron density increased by increasing laser pulse energy due to the laser peak energy that increased the likelihood of ionization collisions with increasing electron energy in all metals. The electron temperature is heavily dependent on the laser's peak power as the latter is the source of evaporation, atomization, and concentrated ionization of the target [8].

Figure 2. Plasma emission spectroscopic pattern for pure target Zn at different laser energy sources.

Figure 3. Plasma emission spectroscopic pattern for pure target Mn at different laser energy

Figure 4. Plasma emission spectroscopic pattern for pure target Se at different laser energy sources
Tables (1, 2 and 3) show the calculated electron temperature, electron density and plasma frequency for the target of zinc, manganese and selenium at different laser energies. All calculated plasma parameters correspond to the plasma conditions and criteria. Plasma was achieved through the results of the plasma parameters ($\lambda_D, f_p, n_e$). This result is in agreement with [9].

| Laser energy (mJ) | FWHM (nm) | $T_e$ (eV) | $n_e$ (cm$^{-3}$) | $f_p$ (Hz) | $\lambda_D$ (cm) | $N_D$ |
|-------------------|----------|-----------|------------------|-----------|-----------------|-------|
| 650               | 2.70     | 0.021     | 7.08E+17         | 7.6E+12   | 1.3E-07         | 6.0E-03 |
| 750               | 3.00     | 0.021     | 7.87E+17         | 8.0E+12   | 1.2E-07         | 5.9E-03 |
| 850               | 3.10     | 0.022     | 8.13E+17         | 8.1E+12   | 1.2E-07         | 6.3E-03 |

**Figure (a).** Variation of $n_e$ and $T_e$ plasma emitted from pure Zn target using laser with different energy

**Figure (b).** Variation of $n_e$ and $T_e$ plasma emitted from pure Se target using laser with different energy

**Figure (c).** Variation of $n_e$ and $T_e$ plasma emitted from pure Mn target using laser with different energy
Table (2): Plasma parameters with different laser energies for a pure (Se) target.

| Laser energy (mJ) | FWHM (nm) | $T_e$ (eV) | $n_e$ (cm$^{-3}$) | $f_p$ (Hz) | $\lambda_D$ (cm) | $N_D$ |
|-------------------|-----------|-------------|-------------------|-------------|------------------|-------|
| 650               | 2.60      | 0.736       | 6.82E+17          | 7.4E+12     | 7.7E-07          | 1.3E+00 |
| 750               | 2.70      | 0.777       | 7.08E+17          | 7.6E+12     | 7.8E-07          | 1.4E+00 |
| 850               | 2.80      | 0.797       | 7.34E+17          | 7.7E+12     | 7.7E-07          | 1.4E+00 |
| 950               | 2.80      | 0.821       | 7.34E+17          | 7.7E+12     | 7.9E-07          | 1.5E+00 |

Table (3): Plasma parameters with different laser energies for a pure (Mn) target.

| Laser energy (mJ) | FWHM (nm) | $T_e$ (eV) | $n_e$ (cm$^{-3}$) | $f_p$ (Hz) | $\lambda_D$ (cm) | $N_D$ |
|-------------------|-----------|-------------|-------------------|-------------|------------------|-------|
| 650               | 3.20      | 0.214       | 8.9E+18           | 2.7E+13     | 1.15E-06         | 5.4E+00 |
| 750               | 3.30      | 0.219       | 9.2E+18           | 2.7E+13     | 1.14E-06         | 5.3E+00 |
| 850               | 3.50      | 0.225       | 9.7E+18           | 2.8E+13     | 1.12E-06         | 5.08E+00 |
| 950               | 3.50      | 0.231       | 1.1E+19           | 2.9E+13     | 1.1E-06          | 4.7E+00 |

3.2 Structural characteristics

3.2.1 X-Ray Diffraction

The Diffraction of X-rays results of the figures below (5) were shown for thin films of pure zinc oxide deposited on glass bases at room temperature and by the effect of laser energy (950 mJ). It was observed that it is polycrystalline and has a hexagonal crystal system for Zinc oxide and the preferred growth trend is (002) for which is in good agreement with [10,11]. X-ray diffraction pattern for Mn powder is polycrystalline cubic system and MnO thin film shows an amorphous structure. Whereas the results of pure selenium thin films prepared after the one-hour annealing process were also polycrystalline with a hexagonal crystal system and the preferred growth direction (011) as shown figure (6) and this result is consistent with [12].

Figure (5): XRD patterns of the (ZnO) thin film using prepared PLD technique with number of pulse =100 shots

Figure (6): XRD patterns of the Se thin film prepared using PLD technique and annealed at 373k with number of pulse =100 shots.
3.2.2 Morphological properties

3D AFM images and granularity accumulation distribution chart of (ZnO, MnO and Se) thin films deposited on glass substrate were synthesized with different laser energy and number of shots shown in Fig (7). These figures show that the particle sizes for all atoms are located in the nanometric scale. These Shapes illustrates that the average diameter decreases with increasing number of energies laser this result is in agreement with [13].

**E=950mJ, ZnO, G.S=34.16nm**

**E=950mJ, G.S=46.91nm,MnO**

**E=950 mJ, Se, G.S=45.23nm**

*Figure (7).* 3D AFM and their granularity accumulation distribution thin film prepared by PLD with laser energy and annealed T=373 K for Se and at R.T for ZnO and MnO.

**Conclusions**

1- Laser-induced plasma emission spectral line intensity showed a strong dependence on pulsed laser energy.
2- The XRD characterization indicates that with a hexagonal system, ZnO and Se have wurtzite type polycrystalline thin film, while with a cubic system, MnO has wurtzite type polycrystalline thin film.
3- AFM investigation shows that the average roughness and RMS increase with increasing of the energy, while the average diameter decreases with increasing of the energy.
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References

[1] Wu, B. and Shin, Y.C. "Modeling of nanosecond laser ablation with vapor plasma formation". Journal of Applied Physics. Vol. 99(8) (2006): 084310.
[2] B. Kearton and Y. Mattley, “Laser-induced breakdown spectroscopy: sparking new applications,” Nature Photonics, vol. 2, no. 9, pp. 537–540, 2008.
[3] D. A. Cremers, L. J. Radziemski, and J. Wiley, Handbook of Laser-Induced Breakdown Spectroscopy, John Wiley & Sons, 2006.
[4] A. W. Miziolek, V. Palleschi, and I. Schechter, Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications, Cambridge University Press, 2006.
[5] N. M. Shaikh, Y. Tao, R. A. Burdt, S. Yuspeh, N. Amin, and M. S. Tillack, “Spectroscopic Studies of Tin Plasma Using Laser Induced Breakdown Spectroscopy,” J. Phys. Conf. Ser., vol. 244, no. PART 4, pp. 2–5, 2010.
[6] Samek O., Beddows D., Telle H., Kaiser J., Liska M., Cáceres J. O. and Gonzáles A. “Quantitative Laser-Induced Breakdown Spectroscopy Analysis of Calcified Tissue Samples,” Spectrochemical Acta Part B: Atomic Spectroscopy, vol. 56 (6) (2001): 865-875.
[7] S. Z. H. R. and J. A. Kashif Chaudhary, “Laser-Induced Plasma and its Applications,” RFID Technol. Secur, Vulnerabilities, Countermeas., 2016.
[8] K. A. Aadim, A. Z. Mohammad and M. A. Abduljabbar "Influence of laser energy on synthesizes of CdO/Nps in liquid environment" Conf. Series: Materials Science and Engineering, vol. 454 (2018) 012028.
[9] Baida M. Ahmed, Kadhim A. Aadim and Madyan A. Khalaf "Verify the plasma parameters generated from the Tin material using the laser-induced plasma technique" World Scientific News, vol. 144 (2020):326-337.
[10] Ayad Z. Mohammad, Kadim A. Aadim and May A. Abduljabbar, "Laser Energy Impact on CdO NPs Prepared By PLD Technique", Indian Journal of Natural Sciences, vol. 8 (2018):14106-14111.
[11] Sahar F., Azam M., Mahmood G., "The effect of laser environment on the characteristics of ZnO nanoparticles by laser ablation" International Nano Letters, vol. 6 (2016): 45-49.
[12] Salitra G., Hodes G., Klein E., Tenne R.” Highly oriented WSe2 thin films prepared by selenization of evaporated WO3”. Thin solid films, vol. 245, (1994):180-185
[13] K. A. Aadim, A. Z. Mohammad and M. A. Abduljabbar "Influence of laser energy on synthesizes of CdO/Nps in liquid environment" Conf. Series: Materials Science and Engineering, vol. 454 (2018) 012028.