Chapter #3

Study of Impurities Deposited on Optical Window

Chapter #3

Study of impurities deposited on Optical Window

The optical window is an important component due to its significant role in the diagnostics of the tokamak plasma. Therefore, in the present chapter, the emission spectra from the laser induced plasma of the optical window of Aditya Tokamak have been studied to identify the deposited materials on its surface. Different layers of the window such as impurity deposited layer, antireflection coating and main matrix of the window material have been identified. The concentrations of the impurities are also estimated by CF-LIBS approach and we have tried to explain the sources of impurities deposited on its surface. Principal component analysis (PCA) using LIBS data is performed to differentiate the different layers (Impurity, Antireflection coating and Main matrix) of the window.

3.1 Sample Collection & Experimental Setup

Optical window (Figure 3.1) of Aditya Tokamak [1] was brought from Institute for Plasma Research (IPR), Gandhinagar, Gujarat, India to Laser Spectroscopy Research Laboratory, Department of Physics, University of Allahabad, U.P., India. This optical window was installed in the tokamak vacuum vessel, thus exposed side of the window is exposed to the plasma generated eroded material in the tokamak. Due to plasma-wall interaction, some material from the wall is eroded and finally deposited on other cooler area of the vacuum vessel like the optical window and other view ports. The optical window was exposed to ~ 400 tokamak plasma discharges and also, the window remained exposed to the pulsed plasma discharge cleaning of the tokamak.

The experimental arrangement as shown in Figure 3.2 was used to record the LIBS spectra of the optical window at different depths and at different locations [2-5]. It consists of a laser source, a rotational stage (Sandvic Components, India) placed on jack (Sandvic Components, India) to have concentric rotation of the sample and a spectrometer with detector (Figure 3.2). The laser source was a frequency-doubled Nd:YAG laser (532 nm) (Continuum Surelite III-10) capable of delivering a maximum energy of 425 mJ with a pulse duration of 4 ns (full-width at half-maximum) with a maximum pulse repetition rate of 10 Hz. In the present experiment, a plano-convex lens with focal length 30 cm was used to focus the laser beam onto the window surface. The emission from plasma was collected at an angle of 45° to the incident laser beam using a collecting lens (fused silica) coupled with optical fiber bundle (having attenuation of 0.8-0.05 db/m in spectral range 200-400 nm and below 0.05 db/m in the spectral range 400-
900nm) and was fed into the spectrometer (Ocean Optics, LIBS 2000+) equipped with a charge-coupled device (CCD).

Figure 3.1: Photograph of (a) exposed/inner and (b) unexposed/outer part of the optical window.

Figure 3.2: Experimental arrangement for recording the LIBS spectra of the optical window.

The spectral range of the spectrometer is 200-980 nm and slit width is 5 μm. Total of 14336 pixels are available in the CCD with pixel size 6μm X 6μm. The sample was rotated mechanically to get fresh spot of the sample for every laser shot. All the experiments have been performed in open atmosphere. The resulting spectra were analyzed using OOI LIBS 2000+ software. The LIBS spectra were collected at 1.5 μs gate delay to eliminate plasma continuum effects. The laser pulse energy was optimized and the best signal to background ratio and signal to noise ratio was observed with energy of
15 mJ. The laser pulse energy was measured with an energy meter (Genetec-e model UP19K- 30 H-VM-DO). To measure the instrumental width of the spectrometer, we have used Hg-Ar calibration source (Ocean optics) and the calculated value is 0.05 nm [5]. The LIBS spectra of different portions of the sample were recorded using a spectral resolution of 0.1 nm in the spectral range 200–500 nm and a spectral resolution 0.75 nm in the spectral range 200–900 nm [5]. The spectral response of all the channels of the present spectrometer is almost constant.

In present chapter, our aim is to identify the impurities/contaminants distributed spatially in the different layers of the optical window. For this purpose, we have recorded the single laser shot LIBS spectra by focusing successive laser shot at the same point and similar experiment have been performed at different points in a concentric circles. A suitable arrangement was made to rotate the window so that every laser shot fall in the periphery of the same circle. In this way the LIBS spectra of exposed and unexposed surface (Figure 3.1a-b) of the optical window have been recorded.

3.2 Result and Discussion

3.2.1 Depth profile analysis of exposed/inner (facing towards plasma) surface of the optical window

For detailed analysis, single shot LIBS spectra of exposed surface of the optical window have been recorded and it is shown in Figure 3.3. Spectral lines have been identified using the National Institute of Standards and Technology (NIST) atomic spectroscopic database [6] and W.R. Brode, Chemical Spectroscopy [7]. It is clear from Figure 3.3(a-b) that spectral lines of Cr, Fe, Ni, Mo, Mn, Cu, C and O are present in the LIBS spectra of inner/contaminated surface of the optical window.

Generally two type of materials SS316L and SS304L are used to construct the tokamak vacuum vessel [8]. The SS316L contains Mo whereas SS304L material does not contain Mo [9-10]. Therefore, the presence of Mo as an impurity in the LIBS spectra of exposed surface of the optical window clearly indicate that vacuum vessel wall of the Aditya Tokamak [11] is constructed of SS316L material and a small amount of SS316L material is eroded during plasma wall interaction [4]. The major constituents of SS316L is Fe (61-64%) whereas its minor constituents are C (<0.03%), Cr (16-18.5%), Ni (10-14%), Mo (2-3%), Mn (<2%), Si (<1%), P (<0.045%), S (<0.03%) and N (0.1%) [9-10]. Content of C in SS316L is very small (<0.03%) thus presence of C in LIBS spectra of
impurity layer might be related to erosion of carbon from the limiter, which is made up of graphite and used as tokamak wall protector from burning plasma.

Figure 3.3: A typical LIBS spectra indicating impurities present in exposed/inner surface of the window in spectral range (a) 250-300 nm and (b) 300-350 nm.

Figure 3.4: Variation of intensity of spectral lines of Fe (438.3 nm), Cr (428.9 nm) and Ni (345.8 nm) with successive laser shots focused at same point of exposed surface of the window.

For depth profile analysis of impurity elements, LIBS spectra of impurity layer have been recorded with successive number of laser shots. For this purpose, 12 laser shot have been focused at the same point of the window and recorded the LIBS spectra for
each laser shot. We have measured the intensity of spectral lines of Fe (438.3 nm), Cr (428.9 nm) and Ni (345.8 nm) with the successive laser shots. Such measurements were repeated for 10 points that lie in a circle and the average intensity of the atomic lines for Fe, Cr and Ni as a function of increasing number of laser shots are plotted in Figure 3.4. Figure 3.4 shows that the intensity of atomic lines of Fe (438.3 nm), Cr (428.9 nm) and Ni (345.8 nm) drastically decreases with increasing number of laser shots and become almost zero after 6th laser shot. This result shows that a very thin layer of impurity is deposited on the exposed surface of the window.

Figure 3.5 shows the intensity variation of atomic lines of Mg (279.5 nm) and Ca (422.6 nm) with number of laser shots in the LIBS spectra of exposed surface of the optical window. In the case of Mg, its intensity is lower in first laser shot and it increases in the 2nd laser shot and thereafter it starts decreasing and becomes almost zero after 6th laser shot. But, the intensity of Ca line decreases drastically starting from 1st laser shot and becomes almost zero after 6th laser shot.

Less spectral intensity of Mg at first laser shot LIBS spectra indicates that it is not related with impurity elements. But it is related with some type of coating which is present below the impurity layer. It may be the antireflection coating (generally coated to avoid reflections) layer containing Ca and Mg. Here, the spectral intensity of Ca decreases from first laser shot which indicate that the antireflection coating is of two type one coating containing Mg followed by another coating containing Ca. Thus behavior of Ca and Mg show that coating layer on optical window containing Ca and Mg is very thin and it is below the impurity deposited layer. Due to the presence of impurity layer, less amount of coating layer is ablated in the first laser shot, therefore in case of Mg, the intensity first increases then decreases with number of laser shots. The Ca containing layer is present in between the Mg layer and impurity layer and in first laser shot along with the impurity material sufficient material of Ca laser is ablated therefore its trend with successive laser shot is normal. The presence of two different antireflection coating will be confirmed in next sub-section.
Figure 3.5: Intensity variation of spectral lines of Mg (279.5 nm) and Ca (422.6 nm) with successive laser shots focused at same point of exposed surface of the window.

Figure 3.6: Intensity variation of spectral lines in different spectral range (a) 245-255 nm and (b) 390-400 nm, with increasing laser shot focused at same point of exposed part of the optical window.

Figure 3.6 shows the variation of spectral line intensities emitted from the exposed surface of the window with increasing number of laser shots [12-13]. All the spectral lines of impurities i.e. the constituents of SS316L are present in first laser shot, but in third laser shot most of them have either disappeared or appeared with reduced intensity than the first laser shot spectra. After 5-6 laser shots, the spectral lines related to the impurities completely disappeared. It can be seen that after a few laser shots at the same
point, spectral lines related to new elements (Si, B and Al as shown in Figure 3.6 a-b) start appearing which may be related to the main matrix of the optical window.

3.2.2 Depth profile analysis of unexposed/outer surface of the window

To confirm the above fact of new appearing lines, we have recorded the LIBS spectra of unexposed surface of the window. The LIBS spectra (Figure 3.7) show the presence of spectral signature of Si, B, Al, Ca and Mg on its unexposed surface. Spectral signature of Fe, Cr, Ni, Mn, Mo and Cu are absent in the LIBS spectra (Figures 3.7) of the unexposed/outer surface of the optical window because this surface is not in contact with the plasma of the tokamak.

![Intensity variation of spectral lines with increasing laser shot focused at same point of unexposed part of the optical window in wavelength range 200-510.](image)

It is clear from Figure 3.7 that Ca and Mg are present at first laser shot spectra and after 2-3 laser shots their spectral lines completely disappear which shows that Ca and Mg are not the matrix elements of the window. Therefore Si, B and Al are the matrix elements of the optical window. These are the same elements which were related to the new appearing spectral lines in exposed surface of the window (Figure 3.6) and hence our assumption was true that the new appearing lines are the matrix elements of the window.
Chapter #3  Study of impurities deposited on Optical Window

Figure 3.8: Intensity variation of spectral lines of (a) anti-reflection coating Ca (422.6 nm) and Mg(279.5 nm) with successive laser shots at same point unexposed/outer surface of the window and the corresponding spectra in spectral range (b) 391-398 nm and (c) 279-289 nm.

The presence of spectral signature of B, Al and Si confirms that it (window) is made up of Boro-aluminosilicate glass. Presence of spectral signature of Ca and Mg in the LIBS spectra (Figure 3.8b-c) of unexposed/outer surface is due to antireflection coating on the optical window [14]. To confirm the above observation, we have recorded the LIBS spectra of the unexposed surface by focusing the laser beam at one point and measured the signal intensity after each laser shot. The variation in intensity of the spectral lines of Ca and Mg with increasing number of laser shots in the LIBS spectra of the unexposed surface of the window are shown in Figure 3.8(a-c).

Here the intensity of the spectral lines of Ca are maximum in the first laser shot and after this shot it rapidly decreases and become approximately zero after 2nd/3rd laser shots (Figure 3.8a). However, in the case of Mg the intensity becomes approximately zero after 4th laser shot (Figure 3.8a). It again confirms that there are two type of antireflection coating. At first there is an antireflection coating containing Mg and then over this
coating there is another coating of material containing Ca. It is expected that after a few laser shots, the coating (containing Ca and Mg) have been removed. Due to this, the intensity of spectral lines of Ca and Mg decrease whereas the intensity of spectral lines of main matrix elements (Si, B and Al) of the material of the window increases with increasing laser shots, such variation for Si is shown in Figure 3.8c. Thus our experimental result show that the antireflection coating of Ca is very thin and just below there is a thin layer of Mg coating on the optical window.

We have also measured the intensity of the spectral lines of Al, B and Si after every successive laser shots and plotted as shown in Figure 3.9. The spectral line intensity of Si, Al and B increases with increasing laser shots and becomes approximately constant after few laser shots (Figure 3.9). It is also observed that up to 4th - 5th laser shot, the increase in intensity is large and later the change is slow and finally become approximately constant. This indicate that after 4th laser shots laser reaches to the matrix of the window and in the 5th laser shot the ablated material gives only the spectral signature of the matrix elements of the window.

Table 3.1: Spectral lines present in the LIBS spectra of exposed surface of the optical window

<table>
<thead>
<tr>
<th>Elements related to impurity layer</th>
<th>Elements</th>
<th>Wavelengths of spectral lines (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td></td>
<td>252.2, 271.9, 278.8, 344.0, 358.1, 371.9, 373.4, 374.5, 374.9, 375.8, 382.0, 385.9, 404.5, 438.3, 234.3, 238.2, 239.5, 240.4, 249.3, 258.5, 259.8, 261.1, 273.9, 274.9, 275.5</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>357.8, 359.3, 360.5, 425.4, 427.4, 428.9, 205.5, 206.1, 206.5, 283.5, 284.3, 286.2</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>300.2, 301.2, 305.0, 313.4, 341.4, 344.6, 345.8, 346.1, 349.2, 351.5, 352.4, 356.6, 361.9, 216.5, 217.4, 220.6, 221.6, 227.0, 231.6</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td>313.2, 319.3, 379.8, 406.9, 418.8</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td>199.9, 279.4, 403.3, 257.6, 293.9, 344.1</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>216.5, 324.7, 327.4</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>247.8, 229.6</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>313.4, 407.5, 441.4</td>
</tr>
</tbody>
</table>

Elements related to antireflection coating layer

| Ca                                |          | 422.6, 445.4, 317.9, 373.6, 393.3, 396.8 |
| Mg                                |          | 279.0, 279.5, 279.8, 280.2 |

Elements related to main matrix of the Optical window

| Si                                |          | 221.1, 221.6, 250.6, 251.6, 251.9, 252.4, 288.1 |
| Al                                |          | 236.7, 237.3, 308.2, 309.2, 394.4, 396.1 |
| B                                 |          | 208.8, 249.7, 239.5, 345.1 |
Figure 3.9: Intensity variation of spectral lines of Si (288.15 nm), Al (309.27 nm) and B (249.678 nm) with successive laser shots focused at same point of unexposed/outer surface of the window.

Now after the complete elemental analysis of different parts of the optical window, the elemental profile of different parts are tabulated as shown in Table 3.1. Now in this way, with the help of LIBS technique, we have successfully identified four different layers on the surface of optical window.

3.2.3 Calculation of concentration of constituents of the optical window using CF-LIBS

We have also tried to measure the concentration of impurities deposited on the optical window. In the present chapter calibration free LIBS (CF-LIBS) technique has been used for estimating the concentration of above elements [15-17]. But before using the LIBS data for CF-LIBS method, there are three conditions/assumptions which should be satisfied; (i) laser ablation should be stiochiometric (ii) plasma should be in local thermal equilibrium, and (iii) the plasma should be optically thin [15, 18-19]. These assumptions have been verified as discussed below.

3.2.3.1 Stoichiometric ablation

The laser produced plasma should truly represent the composition of sample i.e. the ablation should be stoichiometric in nature. If the laser irradiance is greater than 10^9
W cm\(^{-2}\), it does not produce much vaporization; instead only an explosion of the material takes place from the target surface [20]. Since the laser flux density is very high, the ejected material is further heated by absorption of incoming laser radiation and finally produces laser induced plasma. Thus in this case the resulting plasma is stoichiometric [21-22]. Spot size (D) of the laser on the surface of the sample can be calculated using 
\[ D = \frac{4\lambda f}{\pi d} \]
where \(\lambda\) is the wavelength of laser, \(f\) is focal length of the lens and \(d\) is the beam diameter of the laser. In the present experiment, laser energy (E) = 15 mJ, \(\lambda = 532\) nm, \(f = 30\) cm and \(d = 9\) mm and the calculated spot size/diameter will be equal to \(22.6\) µm. Hence the fluence and irradiance will be \(3.75 \times 10^3\) J/cm\(^2\) and \(9.37 \times 10^{11}\) W cm\(^{-2}\) respectively. Thus in the present experiment, laser irradiance is greater than \(10^9\) W cm\(^{-2}\) and therefore the condition for stochiometric ablation is satisfied [5, 21].

### 3.2.3.2 Local thermal equilibrium

The intensity of a spectral line of wavelength (\(\lambda\)) corresponding to the transition between the upper level \(k\) and the lower level \(i\) is given by
\[
I_{\lambda}^{ki} = C_k F A_{ki} g_k \frac{e^{-\left(E_k/k_B T\right)}}{U(T)}
\]
(3.1)

Where \(A_{ki}\) is the transition probability in s\(^{-1}\), \(g_k\) is statistical weight, \(F\) is experimental factor, \(C_k\) is the concentration of a species of elements present in the sample, \(k_B\) is Boltzmann constant and \(U(T)\) is the partition function [19, 23]. The logarithmic of the above equation (3.1) will be
\[
ln \frac{I_{\lambda}^{ki}}{A_{ki}g_k} = -\frac{E_k}{kT} + ln \frac{F C_k}{U(T)}
\]
(3.2)

The partition function for emitting species is defined as \(U(T) = \sum g_k \exp(-E_k/k_B T)\) and to calculate the experimental parameter \(F\), it is assumed that the sum of all species concentration is one [5], i.e. \(\sum C_i = 1\).
Figure 3.10: Boltzmann plot for sample elements of (a) exposed and (b) unexposed part of the window.

The equation (3.2) can be graphically represented by $\ln \frac{I_{ki}}{A_{ki}B_k}$ vs $E_k$ in two dimensional space named as Boltzmann plot shown in Figure 3.10 (a-b), whose slope is related to the plasma temperature by $(-1/K_B T)$ and intercept ($\ln \frac{FC_s}{U(T)}$) is related to the species concentration $C_s$ and the experimental parameter $F$. The calculated plasma temperatures for exposed and unexposed parts of the window are found to be $17579 \pm 521 K$ and $11038 \pm 523 K$ using the Boltzmann plot given in Figure 3.10 (a-b) respectively. It is clear that the plasma temperatures calculated for the different species coincide within the difference of $\pm 3\%$ & $\pm 5\%$ and thus the plasma is characterized by single temperature.

For confirmation of the LTE condition, McWhirter criteria (necessary but not sufficient condition) must be satisfied. And also, the excitation temperature calculated using Boltzmann plot and ionization temperature using Saha Boltzmann plot should be similar (sufficient condition) [5, 24]. The lower limit of electron number density for McWhirter criteria (equation 3.3) is given by

$$N_e \ (cm^{-3}) > 1.6 \times 10^{12} \ T^{3/2} \ (\Delta E)^3$$

(3.3)

The electron density can be calculated by measuring the FWHM ($\Delta \lambda$) of the stark broadened line given by the expression
Ne (cm\(^{-3}\)) \approx 10^{16} \Delta\lambda/2w \quad (3.4)

Here w is electron impact parameter whose value 7.18x10\(^{-4}\) nm and 1x10\(^{-4}\) nm for Ca (422.6nm) and Mg (279.5nm) spectral line respectively are obtained from Plasma Spectroscopy by H.R. Griem [25] and \(\Delta \lambda\) is obtained using the relation \(\Delta \lambda_{\text{True}} = \Delta \lambda_{\text{Observed}} - \Delta \lambda_{\text{Spectrometer}}\). Where \(\Delta \lambda_{\text{Observed}}\) is FWHM of stark broadened line and \(\Delta \lambda_{\text{Spectrometer}}\), is the instrumental width. The values of \(\Delta \lambda_{\text{True}}\) calculated for Ca (422.6nm) and Mg (279.5nm) are 0.17 nm and 0.13nm respectively.

![Lorentzian plot of atomic line of (a) Mg (279.5 nm) and (b) Ca (422.6 nm) present in the LIBS spectra of exposed part.](image)

In the present experiment/study the lower value of \(N_e\) for Ca (422.6nm) and Mg (279.5nm) from equation (3.3) are 2.00x10\(^{16}\) cm\(^{-3}\) and 3.76x10\(^{17}\) cm\(^{-3}\) and the value of \(N_e\) obtained from equation (3.4) and using Figure 3.11 are 1.17x10\(^{18}\) cm\(^{-3}\) and 6.42x 10\(^{18}\) cm\(^{-3}\) respectively, which satisfy the necessary condition for LTE.

The Saha-Boltzmann relation of the ionic/ atomic emission intensity ratio is given by

\[
\ln \frac{i_{ij}^I A_{mn}^I g_m^I}{i_{mn}^I A_{ij}^I g_i^I} = - \frac{(E_{i\text{ion}} - E_i^I - E_m^I)}{k_B T} + \ln \frac{2(2\pi m_e k_B T)^{3/2}}{N_e h^3} \quad (3.5)
\]
Where \( m_e \) is electron mass, \( h \) is Planck’s constant, \( E_{\text{ion}} \) is first ionization potential of the element, \( dE \) is lowering correction parameter, \( E_i^{\text{II}} \) and \( E_m^{\text{I}} \) are upper energy levels of ionic and atomic species of the element having transition probabilities \( A_{ij}^{\text{II}} \) & \( A_{mn}^{\text{I}} \) and statistical weights \( g_i^{\text{II}} \) & \( g_m^{\text{I}} \) [5, 20]

![Saha-Boltzmann plot](image)

**Figure 3.12: Saha-Boltzmann plot for calculating the ionization temperature.**

Using equation (3.5), we have plotted the Saha-Boltzmann curve (Figure 3.12) for impurity element Fe and calculated the ionization temperature, which is equal to \((19085 \pm 365) \text{ K}\). This value is very near to excitation temperature \((17579 \pm 521) \text{ K}\) determined in previous paragraph, with difference of \(~8\%\). This satisfies the sufficient condition for LTE.

3.2.3.3 **Optically thin plasma**

In case of optically thin plasma, there is no self absorption i.e. the emitted photons by the excited atoms are not reabsorbed by similar atoms in the ground state. If the intensity ratio of two interference free emission lines of the same element having similar upper state is equal to the product of ratios of transition probability, degeneracy of upper energy level and inverse ratio of their wavelengths then plasma is said to be optically thin [18-19]. Such ratios for spectral lines of Ni, Cr, Cu, Fe, Mo, Ca and Mg have been calculated and values are shown in Table 3.2. It is clear from the Table 3.2 that the intensity ratios \((I_1/I_2)\) of two spectral lines are approximately equal to the ratio \( A_{1g_1} \lambda_2/A_{2g_2} \lambda_1 \). These results demonstrate that the laser induced plasma in the present study is optically thin.
Table 3.2: Verification of optically thin plasma by comparing the intensity ratios of spectral lines and the values of ratios of $A_{1g_1} \lambda_2/A_{2g_2} \lambda_1$

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity ratio($I_1/I_2$)</th>
<th>$A_{1g_1} \lambda_2/A_{2g_2} \lambda_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-I (346.1/349.2)</td>
<td>0.77</td>
<td>0.82</td>
</tr>
<tr>
<td>Cr-I (359.3/360.5)</td>
<td>1.38</td>
<td>1.30</td>
</tr>
<tr>
<td>Cu-I (324.7/327.4)</td>
<td>1.90</td>
<td>2.03</td>
</tr>
<tr>
<td>Fe-I (374.9/375.8)</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>Mo-I (313.2/319.3)</td>
<td>2.26</td>
<td>2.15</td>
</tr>
<tr>
<td>Ca-II (393.3/396.8)</td>
<td>2.06</td>
<td>1.86</td>
</tr>
<tr>
<td>Mg-II (279.5/280.2)</td>
<td>2.00</td>
<td>2.05</td>
</tr>
</tbody>
</table>

After verifying these assumptions, we can use Boltzmann equation (3.2) for calculating the relative concentration of the constituents/elements present in the target sample.

### 3.2.3.4 Calculation of concentration

The detailed algorithm for calculating the concentration of elements present is given elsewhere [5]. To determine the concentration using equation (3.2), different type of input data like intensity which is obtained experimentally and spectral parameters which are extracted from the relevant literature [6] is required.

The concentration of elemental constituents present in the impurity layer of the optical window of the tokamak has been calculated and percentage concentration of elements present in the impurity layer is tabulated in the Table 3.3. The concentrations of elements in the impurity layer are found to the same proportion as present in SS316L (Table 3.3 & 3.4). These results clearly demonstrate that the high temperature plasma reacts with the wall (SS316L) of the tokamak and ablated materials are deposited on the window.

Table 3.3: Relative concentration of elements present in first laser shot of exposed side of the window

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cu</th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>63.76 ±0.24</td>
<td>13.83 ±0.17</td>
<td>12.30 ±0.31</td>
<td>3.45 ±0.01</td>
<td>1.72 ±0.01</td>
<td>0.65 ±0.01</td>
<td>0.61 ±0.01</td>
<td>0.78 ±0.02</td>
<td>2.57 ±0.12</td>
<td>0.50 ±0.02</td>
</tr>
</tbody>
</table>
Table 3.4: Comparison of concentration of impurity elements to that present in SS316L material

<table>
<thead>
<tr>
<th>Elements</th>
<th>Conc. (%)</th>
<th>Ratio</th>
<th>Conc. (%)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>63.76</td>
<td>1</td>
<td>61-69</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>13.83</td>
<td>0.22</td>
<td>16-18</td>
<td>0.26</td>
</tr>
<tr>
<td>Ni</td>
<td>12.30</td>
<td>0.20</td>
<td>10-14</td>
<td>0.16-0.20</td>
</tr>
<tr>
<td>Mo</td>
<td>3.45</td>
<td>0.05</td>
<td>2-3</td>
<td>0.03-0.04</td>
</tr>
<tr>
<td>Mn</td>
<td>1.72</td>
<td>0.03</td>
<td>2</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 3.4 represents the concentration of Fe, Cr, Ni, Mo and Mn measured by CF-LIBS in impurity layer and corresponding concentration present in SS316L. We have also estimated the relative concentration of Cr, Ni, Mo and Mn with respect to Fe by dividing the concentration of these elements with concentration of Fe and the values are tabulated in Table 3.4. It is again clear from Table 3.4 that the ratio obtained from the LIBS spectra of the impurity layer is very close to the corresponding ratio in SS316L.

In a similar way we have also determined the concentration of elements in the unexposed/outer surface of the window using CF-LIBS and the values are tabulated in Table 3.5. It is clear from Table 3.5 that the concentration of Si is nearly 65% which is main matrix of the window.

Table 3.5: Concentration of elements at first laser shot present in unexposed surface of the window

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>65.56± 0.79</td>
<td>3.72± 0.16</td>
<td>0.06± 0.01</td>
<td>26.02± 1.14</td>
<td>4.41± 0.06</td>
</tr>
</tbody>
</table>

For verification of the matrix elements of the optical window, concentrations of the constituents have been calculated using the LIBS spectra of 9th laser shot in exposed and unexposed surface of the window and it is shown in Table 3.6. It is clear from Table 3.6 that the concentration of the elements (related to matrix) in exposed and unexposed surface are similar and all other elements related to impurity layer and antireflection
coatings are absent. This also verify that at 9\textsuperscript{th} laser shot in impurity layer the laser beam reaches to the main matrix of the window.

Table 3.6: Concentrations (%) of the elements at 9\textsuperscript{th} laser shot in exposed and unexposed part of the window

<table>
<thead>
<tr>
<th>Elements</th>
<th>9\textsuperscript{th} laser shot in exposed surface</th>
<th>9\textsuperscript{th} laser shot in unexposed surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>95.34 ± 1.32</td>
<td>94.85 ± 2.14</td>
</tr>
<tr>
<td>Al</td>
<td>4.58 ± 0.39</td>
<td>5.08 ± 0.47</td>
</tr>
<tr>
<td>B</td>
<td>0.07 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
</tbody>
</table>

3.2.4 Principal component analysis (PCA) of LIBS data

PCA of LIBS data enables us to classify & differentiate the different samples as well as different portion or layer of the same sample [2]. Statistical method such as PCA is expected to play a major role in LIBS-based discrimination of LIBS spectra of different layer of the optical window [26]. PCA program (Unscrambler 10.1, Camo India Pvt. Ltd.) and LIBS data (spectral intensity and wavelength) was used for the classification. The detailed algorithm used in PCA program is given in the reference [2, 26].

![PCA plot](image)

Figure 3.13: PCA plot for single shot of exposed and unexposed part of the window.

The data matrix of wavelength and intensity of LIBS spectra (16 x 5851, having spectral information of exposed and unexposed side of the window) was fed to PCA program which gives the PCA plot shown in Figure 3.13. From Figure 3.13, one can see that the LIBS data points (u1) related to unexposed surface of the window have been
clustered i.e. points are placed very close to each other while the LIBS data points (e1) related to exposed side of the window are relatively far/separated from each other. The reason for such variation in PCA of the data of two surfaces is because in unexposed surface, there is no impurity deposited while in exposed side of the window the impurity material have been deposited and the deposition is not uniform in whole surface of the window. But it is clear from Figure 3.13 that the PCA of the LIBS data of exposed and unexposed side of the window are completely separated from each other. In this way one can quickly identify the exposed and unexposed surface of the window.

To discriminate the different layers (impurity, antireflection coating and main matrix of the window) of the exposed part, LIBS spectra at each points of exposed surface after one laser shot, two laser shot and so on has been used. LIBS data from these spectra were used to get matrix of 71x5851. This matrix was solved using PCA program which gives PCA plot shown in Figure 3.14. From Figure 3.14, it is clearly seen that the PCA plot for one laser shot, two laser shot, three, four and five laser shot are separated completely. The LIBS data points in PCA plot after 5 laser shot are clustered together which show that the LIBS data points are same after 5 laser shots because after 5 laser
shot, the impurity material is completely removed which is also revealed from Figure 3.5. After 5 laser shot the material from the main matrix of the window is ablated therefore the LIBS spectra recorded after 5 laser shot are very similar to each other and thus LIBS data points are merged after 5 laser shot (Figure 3.14).

![PCA plot for shot wise variation of unexposed part of the window.](image)

Similarly, we have also prepared the matrix of 101x5851 from the LIBS spectra of one laser shot, two laser shot and so on at the same point of unexposed surface of the window. This matrix has been solved using PCA program, and the PCA plots are shown in Figure 3.15. Again it is clear from the Figure 3.15 that LIBS data point for first laser shot formed one cluster where as the data set of two laser shot, three laser shot and onwards formed another cluster and the data points are merged together. This is because, in upper layer of the unexposed surface of the window, there is an antireflection coating which is almost removed after one or two laser shot and the spectral feature after one laser shot is similar because the material of the main matrix of the window is ablated after one shot and giving similar spectra that reflect the same in PCA analysis shown in Figure 3.15.
3.3 Conclusion

The present chapter reveal that a thin layer of impurity elements like Fe, Cr, Ni, Mo, Cu and Mn which are the constituents of the material (SS316L) used for the construction of tokamak vessel, along with C (eroded from limiters) were deposited on the optical window. Deposited impurity layer is very thin (few µm) because after 5-6 laser shots, the deposited impurities are removed and the intensity of the spectral lines belonging to impurities is drastically decreased. The experimental result of the present study show that the single shot LIBS spectra is suitable to analyze the elements present in different layers of the optical window. Spectral signatures of B, Si and Al are seen in the LIBS spectra of unexposed surface of the optical window and their intensities increases with increasing number of laser shots indicating that B, Si and Al are the main matrix elements of the optical window. The spectral signature of Ca and Mg are also seen and their intensities are drastically decreased after 1<sup>st</sup>/2<sup>nd</sup> laser shots in unexposed surface, while such type of decrement is observed after 5 laser shots in exposed surface of the optical window. The results indicate that a thin layer of antireflection coating is present just below the layer of impurities on the exposed side of the window whereas the antireflection coating is at the top surface of the unexposed surface of the window. Thus on the basis of LIBS spectral analysis, it is concluded that the optical window of the tokamak is made up of matrix elements (Si, Al and B) then there is an antireflection coating containing Mg then antireflection coating containing Ca. A thin layer of impurity materials (Fe, Ni, Cr, Cu, Mo, Mn, C, O etc.) is deposited on the exposed surface of the window, while on outer/unexposed surface only the antireflection coating is present.

The concentrations of impurities are calculated using CF-LIBS and the concentration obtained are in good correlation with concentration of the constituents of SS316L material which is used for construction of the wall of the tokamak. PCA analysis using LIBS data clearly classify the different layers of the exposed and unexposed part of the window.
References:


