

Data Analysis of Optical Emission Spectroscopy: A DC Reactive Magnetron Sputtering of Titanium Dioxide Case

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Abstract—An alternative approach for data analysis of optical emission spectroscopy was developed to overcome the dilemma of the low emission intensities and high sensitivity of the reconstruction on small errors of the line intensities. This work comprises of data analysis of an experimental dc reactive magnetron sputtering of titanium dioxide. The proposed method was based on several works and aimed to provide accuracy improvement of the method commonly employed in commercial systems. The wavelength calibration can be carried with the ease and without having to write calibration coefficients on the EEPROM. More accurate peak finding was obtained by coupling spectroscopic raw data processing with a Lorentzian line broadening and recognizing technique. The results are displayed with the advantages of the proposed method.

Keywords —OES, wavelength calibration, spectroscopic raw data, Lorentzian lineshape, titanium dioxide

I. Introduction

Optical emission spectroscopy (OES) is a well-established, noninvasive technique of plasmas applied to identify excited and ionized species during discharge deposition [1-4]. However, OES generally measures integrated emission or emission from a limited zone of plasmas. Most diagnostic methods involve the emission spectra from atomic or molecular species in conjunction with fundamental equations which are derived from Boltzmann, Saha or other equilibrium relationships [4-5] based on coronal model [6-7].

Signature of these species [The impinging particles can be the molecules, energetic ions and neutrals] could be identified through in situ investigation using OES [8].

Several works has adopted approaches for monitoring specimens, intensity of selected lines or combinations of intensities or intensity ratios [9-15].

A vast different of selected lines were chosen for a single species. This is no surprise since the differences in deposition condition such as pressure, power and deposition current and etc. [16]. However, agreement between different laboratories is often dependent on the exact plasma operating conditions.

OES is a powerful plasma measurement tool, but also very complicated analysis technique especially where emission intensity can weakling reaches the measurement system. The emission intensity of the optical wavelength being measured is a convolution of the species density, the electron distribution function and the cross-section of excitation of the optical level [17].

The emission wavelengths are accurately identified fingerprint of the species in the plasma due to the energy levels of various atoms and molecules are quite well documented.

The OES instruments are also very sensitive and high degree of accuracy for atomic analysis can only be achieved with a good calibration of the equipment and its resolution [18]. Commonly, wavelength calibration from commercial systems is based on polynomial models. It is interesting to explore an alternative curve fitting methods base on models such as Fourier or Gaussian models for exploring the possibility of accuracy improvement.

Moreover in commercial systems, the spectra are usually pre-processed with smoothing of the acquired data by filtering or other smoothing tools. This leads to observable errors into the peak finding due to the high sensitivity of the reconstruction on small errors of the line intensities. Dotd and Dinklage [19] have stated the critical of the problem and they proposed data analysis approach based on previous work by Fischer and Dose [20] which is extended by a direct modeling of spectroscopic raw data rather than an analysis of pre-analyzed line intensities.

This work purposes alternative methods for OES data analysis based on several works on wavelength calibration and analysis of spectroscopic raw data applied on experimental OES results measured from a deposition of titanium dioxide. The peaks on OES spectra are identified and spectra are reconstructed based on a Lorentzian line broadening model. The results have demonstrated the validity of the proposed method with proven advantages. on accuracy improvements as well as the convenient of use of the methods.

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II. Experimental method

The DC magnetron sputtering system for the study is described in detail [21], along with the experiment arrangement for depositions. Briefly the system can be described as a home built reactive DC magnetron sputtering having reactor chamber of 31 cm in diameter. The magnetron system cathode was constructed with cylindrical core magnet and the outer ring shaped cylindrical magnet with residual induction (Br) of approx 14.0 kG. The target is metallic titanium disc (99.97% purity, Kurt J. Lesker) with 54 mm in diameter. Sputtering argon gas (Ar, 99.999% purity; TIG, Thailand) was controlled flow rate of 3 sccm. The base pressure was at approx. 0.001 Pa (1.0×10^{-5} mbar). During sputtering, the sputter pressure and the discharge voltage were kept at 0.4 Pa (4.0×10^{-3} mbar) and 400 volts; respectively, for all measurements while the discharging currents were set to 500, 700 and 1000 mA.

Optical spectra were obtained through a quartz view port using an Ocean Optics, Model USB 4000 spectrometer to gather the data over a range of wavelengths 177.25 nm through 886.52 nm. Wavelength calibration was carried out with Cal2000 from Ocean optics.

The spectral line broadening based upon Lorentz model of line broadening was employed to construct the measured OES spectrum using the experimental amplitudes and width a half-power maximum [19].

Due to complicate spectral lines, only certain dominate lines in the spectrum were selected for spectrum reconstruction. Lines with sufficient intensity and peak shape; above a setting threshold, were extracted from spectrum data. In order to produce a good fit between the profiles and the experimental profiles generated from the spectrometer, close observations on the spectrum where multiple overlapping lines occur were carried out by electronically expanding the specific range of spectrum.

Peak identification was based on NIST database [18]. A Matlab code was implemented to find and extract Ti, Ar and O lines in the forms of element and ion according to from NIST database. Also the reconstructions of spectral lines were implemented with a Matlab code, with the results compared with PLASUS Specline version 2.13.

-Spectroscopic raw data processing with background correction for a signal with peaks by following the process: 1) estimates the background, 2) regresses the varying baseline to the window points using a spline approximation, and 3) adjusts the background of the input signal Y.

-Finds relevant peaks in a noisy signal by peak detection from Matlab

Three wavelength calibrations with good fitting were studied and presented as following:

The wavelength as suggested in the company was based on the relationship between pixel number and wavelength in a third-order polynomial:

$$\lambda_p = I + C_1 p + C_2 p^2 + C_3 p^3$$

where λ_p is the wavelength of pixel p, I is the wavelength of pixel 0, C₁ is the first coefficient (nm/pixel), C₂ is the second coefficient (nm/pixel) and C₃ is the third coefficient (nm/pixel).

We purposed the used of the measured wavelengths instead of using pixel number for calibration. This provided two advantages. The first advantage is measurements can be carried out with factory setting values for calibration

coefficients. This gets rid of the need to write to the new calibration coefficients to EEPROM every time a new calibration is needed. Moreover, the calibration procedure requires user to perform a tedious task in identifying each pixel corresponding to the peak of the reference source. The wavelength calibration based on curve fitting to a predefined-model can be done easily on a simple computer. Secondly, calibration to different light sources for better accuracy when accessible can be carried out at convenient time since the calibration is carried out in form of data analysis with the known wavelengths of the reference light source.

A. Fourier Curve Fitting

General model n-order Fourier is in the form:

$$f(x) = a_0 + a_1 \cos(x*w) + b_1 \sin(x*w) + a_2 \cos(2*x*w) + b_2 \sin(2*x*w) + a_3 \cos(3*x*w) + b_3 \sin(3*x*w) + \dots + a_n \cos(n*x*w) + b_n \sin(n*x*w)$$

The coefficients of the model can easily be obtained by numerical software such as Matlab, by fitting the set measured wavelengths to the reference wavelengths of the calibration source.

B. Gaussian Curve Fitting

General model N-order Gaussian is in the form:

$$f(x) = a_1 \exp(-((x-b_1)/c_1)^2) + a_2 \exp(-((x-b_2)/c_2)^2) + a_3 \exp(-((x-b_3)/c_3)^2) + \dots + a_n \exp(-((x-b_n)/c_n)^2)$$

The coefficients of the model are again can easily be obtained by a numerical software such as Matlab.

Where:

x = the measured wavelength

f(x) = the corresponding calibrated wavelength

C. Peak finding with Lorentzian line broadening recognizing

Lorentzian line broadening

$$\phi(v) = 1/\pi (\alpha L / (v-v_0)^2 + \alpha L^2)$$

where the peak finding involves finding the peak intensity higher than the setting threshold of noisy background and then determined score similarity essentially from normalized dot-product against a specific shape (Lorentzian line shape).

III. Results and Discussion

Table 1 Shows comparison of wavelength calibration with different methods.

It is seen in table 1 showing results from 3 wavelength calibration methods; Commercial, Fourier and Gaussian methods respectively. NIST wavelength in nm was obtained from National Institute of Standards and Technology, Gaithersburg, MD, U.S.A. [18]. With the calibration light source was Cal2000 from Ocean optics. The calibration light source comprises of emission spectra of two atomics; Hg and Ar. It can be observed from the results that for the Fourier model a reasonable calibration was reached from the 1st order of the model. The better results than the suggested commercial method were obtained by the 2nd order.

A good result for the Gaussian model is; however, only reached with the 7th order. This indicates that the Fourier model might be a good choice for the wavelength calibration and the 2nd order is sufficient.

TABLE I . SHOWS COMPARISON OF WAVELENGTH CALIBRATION WITH DIFFERENT METHODS

NIST		Calibration methods										
Wavelength (nm)	Measured wavelength	$\Delta\lambda$	Commercial method	Fourier1	Fourier2	Fourier3	Gaussian7	$\Delta\lambda$	$\Delta\lambda$	$\Delta\lambda$	$\Delta\lambda$	$\Delta\lambda$
			λ_C	λ_{F1}	λ_{F2}	λ_{F3}	λ_{G7}					
253.652	253.450	-0.202	253.704	0.052	253.625	-0.027	253.612	-0.040	253.657	0.005	253.675	0.023
296.728	296.710	-0.018	296.725	-0.003	296.637	-0.091	296.657	-0.071	296.681	-0.048	296.618	-0.110
302.150	302.270	0.120	302.262	0.112	302.172	0.022	302.201	0.051	302.227	0.077	302.180	0.030
313.155	313.140	-0.015	313.091	-0.064	312.999	-0.156	313.043	-0.112	313.078	-0.077	313.063	-0.092
334.148	334.360	0.212	334.249	0.101	334.152	0.004	334.227	0.079	334.274	0.126	334.320	0.172
365.015	365.070	0.055	364.903	-0.112	364.800	-0.216	364.910	-0.106	364.963	-0.052	365.035	0.020
404.656	404.800	0.144	404.613	-0.043	404.501	-0.156	404.628	-0.028	404.666	0.010	404.656	0.000
407.783	407.900	0.117	407.714	-0.069	407.600	-0.183	407.728	-0.055	407.764	-0.019	407.746	-0.037
435.833	436.040	0.207	435.870	0.037	435.750	-0.083	435.868	0.035	435.886	0.053	435.827	-0.006
546.074	546.210	0.136	546.218	0.144	546.074	0.000	546.087	0.013	546.101	0.027	546.083	0.009
576.960	577.010	0.050	577.073	0.113	576.922	-0.039	576.925	-0.035	576.954	-0.006	576.943	-0.017
579.066	579.140	0.074	579.207	0.141	579.055	-0.012	579.058	-0.008	579.088	0.022	579.063	-0.003
696.543	696.420	-0.123	696.537	-0.006	696.358	-0.185	696.523	-0.020	696.548	0.005	696.532	-0.012
706.722	706.670	-0.052	706.772	0.050	706.591	-0.131	706.777	0.055	706.798	0.076	706.744	0.022
727.294	727.200	-0.094	727.258	-0.036	727.072	-0.222	727.293	-0.001	727.308	0.014	727.316	0.022
738.393	738.370	-0.023	738.396	0.003	738.208	-0.185	738.441	0.048	738.455	0.062	738.406	0.013
750.387	750.370	-0.017	750.356	-0.032	750.165	-0.222	750.404	0.017	750.418	0.031	750.346	-0.041
763.511	763.530	0.019	763.463	-0.049	763.269	-0.242	763.503	-0.008	763.518	0.007	763.527	0.016
772.376	772.380	0.004	772.272	-0.104	772.076	-0.300	772.298	-0.078	772.315	-0.061	772.372	-0.004
794.818	795.170	0.352	794.936	0.118	794.736	-0.082	794.885	0.067	794.906	0.088	794.794	-0.024
800.616	801.080	0.464	800.808	0.192	800.607	-0.009	800.726	0.110	800.746	0.130	800.608	-0.008
811.531	811.980	0.449	811.633	0.102	811.429	-0.102	811.478	-0.053	811.494	-0.037	811.556	0.025
SSE:			SSE: 0.161		SSE: 0.1611		SSE: 0.06787		SSE: 0.0666		SSE:0.05805	
RMSE			RMSE: 0.09459		RMSE: 0.09461		RMSE: 0.06513		RMSE: 0.06897		RMSE:0.2409	

* Where λ with subscription indicates the calibration obtained by the corresponding method and $\Delta\lambda$ is the difference from NIST data file.

Acknowledgment

Figure 1 shows a typical example of OES spectrum obtained from the sputtering of titanium dioxide using a dc magnetron sputtering system under a discharging current of 750 mA.

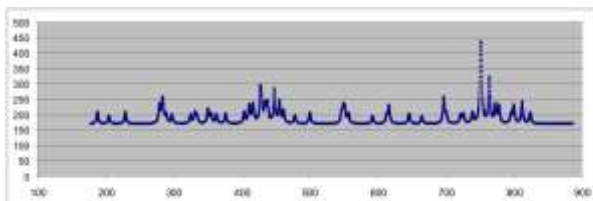


Figure 1. Shows an example of an OES spectrum of a dc magnetron sputtering of titanium dioxide at 750 mA under the deposition condition.

Spectroscopic raw data processing for peak finding with the Lorentzian line broadening recognizing technique was carried out and the result is shown in Figure 2.

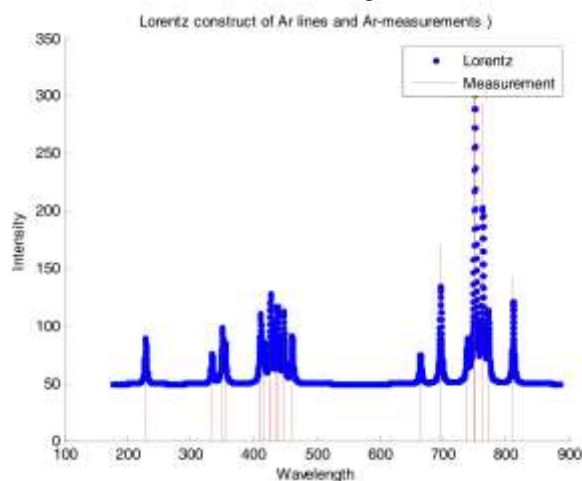


Figure 2. Shows Ar-lines of OES spectrum from a dc magnetron sputtering of titanium dioxide at 750 mA under the deposition condition

IV. Conclusion

An alternative approach for data analysis of optical emission spectroscopy was developed to overcome the dilemma of the low emission intensities and high sensitivity of the reconstruction on small errors of the line intensities. The method was successfully applied to the analysis of experimental data obtained from an OES measurement of a DC Reactive Magnetron Sputtering of Titanium Dioxide. A simpler calibration, based on Fourier curve fitting, but offers a better precision was purposed and as the result it is expected to consequently give a better accuracy on peak finding. Moreover, the method employed a spectroscopic raw data processing [20], in which the error incurred from reconstruction of high sensitivity of intensity can be avoided. The peak finding and reconstructing the integrated with Lorentz line broadening modeling also offer additional accuracy to the technique as also with the good presentation of the spectra. Emission lines from atomics and ions of Ar-sputtering gas, O-reactive gas and Ti were successfully demonstrated as the results.

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