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Hydrogen analysis in diamond-like carbon with glow discharge optical emission spectroscopy

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Abstract

Glow discharge-optical emission spectroscopy (GD-OES) was evaluated for hydrogen analysis in diamond-like carbon (DLC) films. DLC film samples were prepared using plasma-based ion-implantation and deposition method (PBIID). Their hydrogen contents were determined using elastic recoil detection analysis (ERDA). The hydrogen intensity obtained by GD-OES increased gradually concomitantly with increasing hydrogen contents at the lower hydrogen content region. However, the intensity increased drastically at the higher hydrogen content region of more than about 30 at%. When the hydrogen contents increased, the correlation between GD-OES hydrogen intensity and ERDA hydrogen contents was deviated from the linear relation obtained for hydrogen-implanted silicon samples as reference materials. The sputtering rate of the DLC sample was found to vary at high H content region. A linear relationship was obtained between the hydrogen contents and GD-OES intensities corrected with the sputtering rate of samples.

Keywords: GD-OES, DLC, ERDA, hydrogen analysis

1. Introduction

Diamond-like carbon (DLC)[1] has various benefits such as high hardness, low coefficient of friction, and gas-barrier property. In fact, DLC film has attracted much attention for use in industrial parts and devices widely, and recently it has been applied particularly to automotive parts and dies.[2] The DLC film properties depend on its deposition method, condition, and operating environment.[3,4] Various methods have been applied for industrial and laboratory uses. Chemical vapor deposition (CVD) method employs hydrocarbon gas as a precursor material so that the deposited film is fated to involve hydrogen contents of approximately to 50 at%. In contrast, hydrogen-free DLC film is formed using physical vapor deposition (PVD), which uses solid carbon as a precursor material. The DLC film amorphous-carbon network structure is a mixture of sp^3 and sp^2 hybridized orbitals, which respectively indicative the diamond structure and graphite structures. The intrinsic hydrogen content and sp^3/sp^2 bonding ratio are closely related to the DLC film characteristics. Therefore a few groups have proposed a means of classification to organize DLC film characteristics using these parameters.[5,6,7]

Quantitative analysis techniques of hydrogen are limited. E.g., x-ray analysis does not work because hydrogen atoms have no core electron to generate x-ray irradiation and LA-ICP-MS is not applicable because of the air moisture in measurement. LIBS requires inert gas atmosphere. Raman spectroscopy, IR spectroscopy, NMR, EELS, SIMS, and TOF-SIMS provide specific structural

characterization and estimation of hydrogen contents in DLC films. [1] Nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA)[8,9,10]have been widely used for direct hydrogen quantification in DLC films, though they require special facilities. In ERDA, hydrogen atom is struck out of the target sample using an ion beam radiation and then the hydrogen atom energy is detected using solid state detector. The ERDA method enables us to quantify hydrogen contents without reference materials and obtain the depth profiles in the samples surface. However, the method is not available in common laboratories because of its requirement of an ion-beam facility. For that reason, glow discharge optical emission spectroscopy (GD-OES) has been considered for use as a laboratory method instead.[11] GD-OES is an elemental analysis technique for in-depth direction by which the sample sputtering and atomic emission take place simultaneously in an argon plasma atmosphere.[12] The emission intensity is related to the total weight (or total number of atoms) of the element removed per time from the sample material, which enables quantitative analysis. However, for performing quantitative analysis of hydrogen by GD-OES, suitable certified reference materials are under development. Electroplated zinc coatings and carbon-rich hard coating are studied as the potential candidates.[13] Additionally, gaseous elements, such as hydrogen, nitrogen and oxygen are fast reacting with each other and other elements. They are cautioned for some possibility of redeposition in the inner surface of the anode in general.[14] In case, the elemental spectral lines are missed to some extent and band spectra are observed instead. This could cause matrix dependence in

the calibration. Another problem consists of the chemical bonding state and structure in the hydrogen case. If hydrogen exists dissolved in the matrix lattice without proper bonding like a hydrogen storage alloy, the hydrogen atoms could move out fast from the matrix lattice and the sputtering process has an influence on the distribution of hydrogen in the sample. Even though there are such subjects to be solved for performing quantification of hydrogen, GD-OES method has been considered as a practical analysis method for DLC film. The compatibility of GD-OES with ERDA has already been evaluated by two groups for hydrogen quantification of DLC film.[11, 15] They compared GD-OES results to hydrogen contents by ERDA for numbers of DLC film samples prepared with various processes. The measuring depth region is different between GD-OES and ERDA; the measurable film thickness was estimated to about 300 nm for the ERDA, but it was several tens micrometers for GD-OES. The first group reported that GD-OES hydrogen intensities averaged from the top surface to 300 nm depth showed a roughly linear relationship with ERDA hydrogen contents, thought there were several samples deviated from the trend.[11] The second group performed a round robin test on DLC characterization method among several industrial technology institutes in Japan.[15] In their report (not published yet), the GD-OES hydrogen intensities showed not linear but quadratic-like relationship between GD-OES H intensities and ERDA hydrogen contents. Because some sort of relationships were found, GD-OES was proposed as a potential technique for quantitative hydrogen analysis in DLC films in the reports.

In this study, detailed evaluation of GD-OES method was performed for hydrogen analysis of DLC film. The GD-OES profile was analyzed. Then the intensity results were compared with those obtained using ERDA. Several DLC samples were prepared with less than 300 nm thickness appropriate for the measurable thickness of ERDA. Simultaneously hydrogen-implanted silicon was evaluated as a reference material for quantifying GD-OES results. The idea of hydrogen-implanted silicon for reference material has been reported and accepted in temperature programed deposition analysis (TPD).[16] We tried to bring it to hydrogen analysis in GD-OES. The implantation condition was controlled to perform 300 nm in the projected range to measure the entire amount of implanted hydrogen using ERDA.

2. Experimental

DLC films were prepared using plasma-based ion-implantation and deposition (PBIID) method[17]. A PBIID system (Kurita Seisakusyo Co., Ltd.) was available for supplying radio-frequency (RF)-pulse plasma generation and negative high-voltage pulse to the substrate together to perform film deposition and ion-implantation simultaneously. The RF supply was set to 500W in peak power, 50 μs pulse duration, 13.56 MHz frequency, with a 2 kHz repetition rate. Negative high voltage pulse from - 1 to - 10 kV, the duration of 5 μs, and the repetition rate of 2 kHz

were applied to the substrate at 50 μs after each RF pulse. A silicon wafer was used as the substrate. Toluene of hydrocarbon gas was used as the precursor gas. The gas pressure was controlled to 0.7 Pa. The flow rate was set to 30 cm^3 min^{-1}. The uncoated part was left by protecting with a masking tape to evaluate the film thickness using a stylus profilometer as the height gap between the coated and uncoated part.

Hydrogen implantation was performed for the silicon wafer (<100> in crystal orientation) with a H_2^+ source under 30 kV voltage. Then the projected range was estimated to 300 nm with SRIM software based on Monte Carlo calculation method. The target implantation dose was from 5×10^{16} to 10^{18} atoms cm^{-2} by adjusting implantation current (20 -24 μA) and operation time (12 -120 min) for the area of 2×2 cm^2. The sample was tilted at an angle of 7 ° with respect to the perpendicular beam direction to avoid interference by the channel effect.

Prepared DLC films and H-implanted Si wafers were measured using glow discharge optical emission spectroscopy (GD-OES) (GDA750; Rigaku Corp./Spectruma). High purity argon (99.9999%) was used as the discharge gas. Radiofrequency power was applied under the following conditions: 600 V in electric voltage and 300 Pa in gas pressure. The measurement spot was 4 mm diameter. Photomultiplier tubes (PMTs) were used as detector. The following emission lines were applied: H 121.57 nm, C 156.14 nm, and Si 251.51 nm. Molecular spectra were measured with a CCD detector from 215 to 770 nm wavelength and 0.05 nm spectral resolution.

Elastic recoil detection analysis (ERDA) was taken in the Tandem accelerator beam line at The Wakasa Wan Energy Research Center. ^{4}He ions with 2.0 MeV were incident at 10 ° to the sample surface and then the recoiled H atoms are counted by a detector at 20 ° in a forward direction. Simultaneously the C or Si content was measured using Rutherford backscattering spectrometry (RBS) method. The backscattered He ions were counted using a detector at 150 ° against the direction of ^{4}He ion irradiation.

3. Results and Discussion

3.1. GD-OES and ERDA profile analysis for DLC film

The DLC film samples were prepared to have various hydrogen contents by adjusting the deposition conditions.[17] In plasma-based ion-implantation and deposition (PBIID) process condition, increasing negative voltage tends to decrease hydrogen content in DLC film. Alternatively the addition of hydrogen into the precursor gas also decreases the hydrogen content. Table I presents the sample name, deposition conditions and the film thickness. Film samples D1 - D9 were deposited below 300 nm, where ERDA can detect the entire depth region. The samples D10 -D15 were prepared with various practical conditions (300 - 500W RF power, 0.7 - 1.0 Pa gas pressure, -5 – -10 kV negative high voltage pulse) which were different from the conditions for the series of D1 – D9. The D10 – D15 samples have larger thickness so that only the upper region to 300 nm is expected to

contribute to ERDA results.

Figure 1 presents ERDA spectra for the D2 sample. Figure 1(a) displays the yield of recoiled H atoms against the energy. The profile is quantified to the H atomic density as a function of depth from the sample surface based on the simulation result (Fig. 1(b)). The large H content from 0 to about 0.2 μm is assigned to DLC film. The atomic area densities of hydrogen and carbon from the ERDA and RBS fitting results are presented in Table I. The hydrogen content was calculated from the atomic densities of H and C in the fitting result. The hydrogen contents for D1 to D15 samples were determined as given in Table I.

Figure 2 portrays GD-OES profiles for samples D2 and D13. The C, H and Si intensities are shown as a function of the sputtering time instead of the distance from the surface. The upper region composed of C and H is attributed to DLC film. The increase of Si intensity is attributed to the Si substrate. In the vicinity of Si substrate, the C and H intensities are enhanced before decreasing, as presented clearly in Fig 2(b). This is expected to be the result of the DLC which is influenced by the fact that Si which has higher sputtering yield than C has.[18] Moreover the C intensity shows a periodical motion for D2 sample (Fig. 2(a)). When the film thickness is sufficiently thin to be transparent, a certain emission wavelength can conduct interference through reflection from the substrate. In the case of D13 sample, the periodical motion disappears because of its opacity by greater thickness (Fig. 2(b)). Therefore the C intensity variation is not originated from the

concentration variation but from the interference of the emission. The enrichment of C and H on the top surface can result from contamination from the environment, though it was not obvious in the ERDA spectra. Although pre-treatment is useful to clean the sample surface in GD-OES measurement generally, it was not used in this study to have the initial sample surface equivalent in ERDA measurement. The depth resolution in the top surface would be better in GD-OES. The averaged hydrogen intensity was calculated from the plateau intensity and background intensity in each profile. For example, in case of D2 sample shown in Fig. 2 (a), the plateau intensity was averaged between 1.0 and 5.8 s and the background intensity averaged between 15 and 30 s was subtracted from it.

3.2. GD-OES and ERDA profile analysis for H-implanted Si

The H-implanted Si samples with various H contents were measured using GD–OES and ERDA similarly to DLC film samples. Table II gives the sample name and target dose hydrogen. ERDA profile for sample S5 is portrayed in Fig. 3. The ERDA profile exhibits a peak for the implanted hydrogen which is distributed from 50 to 300 nm. Another small peak on the top is well resolved for the surface contamination. Table II presents the atomic area density of hydrogen obtained by ERDA. The surface atomic densities were estimated to $5.9\times10^{16} – 3.3 \times10^{17}$ at cm^{-2} excluding the surface contamination for the samples. The surface atomic densities of the samples are

mostly equivalent to the corresponding target doses less than 1.0×10^{17} at cm^{-2}. But they are likely saturated for the target doses more than 2×10^{17} at cm^{-2}. The atomic density values were converted to atomic contents, assuming that the amounts of H were present in 300 nm depth of Si with theoretical volume density (2.33 g cm^{-3}).

Figure 4 presents GD-OES intensity profiles of H and Si for sample S5. The enrichment of H on the top surface from 0 s to 1.5 s could be attributed to contamination from the environment. The H intensity peak around 4 s is attributed to the implanted hydrogen. The peak structure is attributable to the Gaussian distribution because of the intrinsic characteristics of ion implantation. The peaks spread up to about 6 s for all samples. Referring to the ERDA profile (Fig. 3), the point at 6 s was roughly supposed to 300 nm in depth. This was also supported by the erosion rate (50 – 60 nm s^{-1}), which was estimated from the depth in crater shape after the measurement. Therefore, the peak profile was fitted with a gauss function and the integrated intensity was time-averaged by 6 s for each profile.

3.3. Relationship between GD-OES and ERDA results in DLC film and H-implanted Si samples

Figure 5 displays the relationship between the H content by ERDA and the averaged H intensity in GD-OES for DLC samples. Because H-implanted Si system has different matrix composition

from DLC system, the GD-OES H intensity of H-implanted Si samples was corrected by using the experimental sputtering rate approximately to plot together in Fig. 5, as described below. The sputtering rate was defined as the number of atoms sputtered per unit area and per unit time (at cm^{-2} s^{-1}) where the atomic area density of the matrix element was divided by the sputtering time for convenience. Experimental sputtering rate for H-implanted Si (SR(H-Si)) was estimated to 2.5×10^{17} at cm^{-2} s^{-1} assuming 300 nm depth of Si with theoretical volume density (2.33 g cm^{-3}, 4.99×10^{22} at cm^{-3}) is sputtered by 6 s, as shown in Fig. 4. H peak appeared up to 6 s consistently for the H-implanted Si samples in GD-OES profiles and the sputtering time (6 s) taken for the depth of implantation (300 nm) was almost constant for all H-implanted Si samples. Experimental sputtering rate for DLC (SR(DLC)) was estimated based on the data for sample D4 with the least H contents among the D1-D9 series. The area density of C for D4 was 20.5×10^{17} at cm^{-2} by RBS analyses, shown in Table I. The entire film of D4 is sputtered by 16.7 s in GD-OES (not shown). Therefore the experimental sputtering rate for DLC (SR(DLC)) was estimated to 1.23×10^{17} at cm^{-2} s^{-1}. The SR(H-Si) was high by a factor of 2.0 (2.5/1.23) compared to SR(DLC), so that the H intensities obtained for H-implanted Si samples were divided by the factor (2.0) in Fig. 5.

Regarding to the H-implanted Si samples, the GD-OES averaged H intensity is linearly correlated to ERDA H contents. DLC samples are likely to sustain the linear relation between GD-OES and ERDA at the lower H contents. However, the GD-OES H intensity increased

drastically at more than about 30 at% to enhance the increasing slope. The curve shape was not expressed by the first approximation but by kind of a polynomial or exponential function for the wide H content range. Although we considered H-implanted Si samples to serve as reference samples for DLC film analysis, the DLC result differed from the extrapolation of H-implanted Si result more and more with higher H content region.

The drastically enhancement of GD-OES H intensity at the high H contents was confirmed if it occurred in association with the emission line choice or sputtering rate variation. The monitored optical emission for H analysis is a resonance line at 121.57 nm. The emission characteristics for the individual line, with characteristics such as excitation, absorption, and detailed energy transfers between energy levels, can affect to the intensity variation. For example, the resonance emission line is well known to tend to be saturated with the contents. Another H emission line at 656.28 nm is a non-resonance and visible line of the Balmer series which is related to different energy levels from 121.57 nm. Figure 6 depicts the H emission intensity at 656.28 nm against that at 121.57 nm for DLC film samples. A linear relation appeared between the intensities at 656 nm and 121 nm, suggesting that the incomprehensive increment of H intensity at the high content region would not result from the emission mechanism. In other words, the hydrogen concentration in the plasma would actually increase to raise the H intensity drastically. Figure 7 displays the sputtering rate variation to H contents for the DLC film samples. The sputtering rate was estimated from the

number dividing the total area atomic density of H and C by the sputtering time taken for the whole range in each film sample. The sputtering rate of multicomponents is not explained simply but it is likely related with the mass, atomic radius, binding energy, and other characteristics of the constituents in a general sense.[18] According to these authors, the sputtering rate will have the trend of concomitant increase with increasing H contents considering the smaller mass and/or atomic radius. From the characteristics of DLC too, the hydrogen content is closely related to the sp^2/sp^3 bonding state, density, and structural hardness. It is well-known that the DLC shows tendency to lose the structural hardness by containing hydrogen in general. The decline of structural hardness could bring the enhancement of sputtering rate and the drastically increase of hydrogen intensity for high H contents of DLC.

The sputtering rate enhancement with increasing hydrogen contents in DLC is also in agreement with the experimental results of the molecular spectra measurements. Figures 8 (a) and (b) respectively depict the molecular spectra of C-H and C-C,[19,20,21] which were recorded with a spectrometer equipped with a CCD detector in GD-OES tool. The C-H molecular band structure was observed in the wavelength range of 429-432 nm (Fig. 8 (a)). The C-H band intensity increased concomitantly with increasing H contents in DLC samples, which indicates the formation of CH radical. Additionally, C-C band at 510-570 nm is also strong for higher H containing samples. Two peaks of several peaks in the band are exhibited in Fig. 8 (b), which indicates the formation of CC

radicals also increased with increase of H contents. Figure 9 depicts the intensity dependence on the H contents by ERDA for H peak at 121.57 nm, C peak at 156.14 nm, a representative C-H peak at 430.38 nm and C-C peak at 558.52 nm. The C intensity was almost constant for the H contents, as marked with open circles in Fig. 9, though the C contents decreased instead of increase of H contents. C intensity might be filled by the increase of sputtering rate to have almost constant intensity, further study is necessary to make clear the mechanism. The C-H peak and C-C peak intensities clearly increased with H contents, indicating efficient formation of such fragments by sputtering rate enhancement.

However, "hydrogen effect"[22], which is well-known in GD-OES analysis, should be considered as a supplement reason for to the intensity relationship with H contents. Hydrogen effect modifies the optical emission intensities accompanied with the existence of hydrogen molecule (H_2). This occurs because metastable state of Ar (Ar^m), which has a large contribution to ionization processes, is quenched by collision with H_2 molecule.[23,24] Most analytical lines decrease in emission yields, however some lines are selectively excited. Therefore the intensity dependence of C, C-H peak and C-C peak on H contents might be possible. The further theoretical study is necessary to understand if hydrogen effect could contribute to their intensity changes or not.

Figure 10 plots the GD-OES H intensity corrected by the sputtering rate against the H contents by ERDA for DLC samples. Mostly linear relation between the corrected intensities and H contents

appeared. The sputtering rate variation should be taken into consideration for analyzing hydrogen contents in DLC with GD-OES. Moreover, volatile materials formation, not only of CH and CC but of multiple fragments such as CH_2, CH_3, and C_2H_6 which have poor possibilities for optical emission, is anticipated. Single hydrogen atom emission can be affected if their contributions are too great to ignore. In the lower concentration range below 15 %, further investigation is necessary if the matrix independent calibration of H in Si and C is possible.

Conclusion

Hydrogen analysis using GD-OES was evaluated for DLC films. Several DLC film samples were prepared using PBIID method. Their hydrogen contents were determined with ERDA. The hydrogen intensity obtained by GD-OES was compared with the H contents of the sample using ERDA. No linear relationship between them was found in the results: The GD-OES intensity increased with the H content at the hydrogen content region less than 30 at% but increased drastically at the higher H content region. At the higher H content region, the variation in GD-OES H intensity did not correspond to that for H-implanted Si samples which were regarded as reference materials. The sputtering rate of sample, which was estimated from the atomic density and sputtering time, drastically increase for the high H content region. In the molecular spectra, the formation of volatile material fragments such as CH and CC increased for high H content regions. This suggests

decline of the structural hardness to cause the fast sputtering rate with increase of H contents in DLC samples. By correcting the sputtering rate variation of samples, the GD-OES hydrogen intensity shows linear relationship to the hydrogen contents by ERDA.

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Figure captions

Fig. 1 ERDA spectra for a DLC film sample of D2. The experimental and simulation results are marked respectively with black dots and gray line in energy spectrum of recoil hydrogen (a). Furthermore the quantified result (b).

Fig. 2 GD-OES depth profiles for DLC film samples of D2 (a) and D13 (b).

Fig. 3 Quantified ERDA spectrum for H-implanted Si sample of S5.

Fig.4 GD-OES depth profiles for H-implanted Si sample of S5.

Fig. 5 Relation between the averaged H intensity at 121.57 nm by GD-OES and the H contents by ERDA for DLC film. For H-implanted Si samples, the GD-OES H intensity was corrected by using experimental difference on sputtering rate. The DLC film sample results were distinguished by the thickness below (filled squares) /above (open squares) 300 nm of the ERDA measuring depth to confirm the dependence of thickness.

Fig. 6 Relation between the averaged H intensity at 656.28 nm and 121.57 nm for DLC film samples.

Fig. 7 GD-OES sputtering rate dependence on ERDA H composition.

Fig. 8 Molecular spectra of CH band (a) and CC band (marked with *) (b) for the DLC samples. The lines masked with gray are assigned to Ar peaks.

Fig. 9 GD-OES intensity dependences on ERDA H contents for C 156.14 nm, H 121.56 nm, CH 430.38 nm, and CC 558.50 nm.

Fig. 10 Dependence of the H intensity corrected by the sputtering rate on H contents by ERDA for DLC film samples.

Table I Deposition condition (negative voltage and hydrogen atmosphere) and film thickness for DLC samples. The film thickness was measured with a stylus profilometer. The area densities of H and C were obtained by ERDA and RBS analysis. The hydrogen content was calculated from the ratio of H to total (H + C) area densities.

Sample	Deposition cond.	Thickness (μm)	H area dens. (10^{17} at cm^{-2})	C area dens. (10^{17} at cm^{-2})	H content (at%)
D1	-1 kV	0.086	3.88	7.13	35.2
D2	-3 kV	0.18	5.84	13.2	30.7
D3	-5 kV	0.20	6.28	16.2	28.0
D4	-10 kV	0.19	5.46	20.5	21.0
D5	-10 kV	0.21	5.63	20.4	21.6
D6	H atmosphere	0.15	3.02	9.68	23.8
D7	H atmosphere	0.08	1.52	5.86	20.6
D8	-1 kV	0.29	9.20	19.7	31.9
D9	-1 kV	0.23	6.71	13.8	32.8
D10	-5 kV	0.73	34.4	79.5	30.2
D11	-10 kV	1.44	32.1	160	16.7
D12	-10 kV	4.12	75.4	337	18.3
D13	-7 kV	2.32	38.5	193	16.6
D14	-10 kV	0.94	16.6	77.4	17.7
D15	-10 kV	2.16	36.3	180	16.8

Table II Target dose and the area density obtained ERDA analysis for H-implanted Si sample. H content was calculated from the area density, assuming that H presented in 300 nm depth of Si with theoretical volume density (2.33 g cm^{-3}).

Sample	Target dose H (10^{17} at cm^{-2})	H area dens. (10^{17} at cm^{-2})	H content (at%)
S1	10	3.35	18.4
S2	5	2.62	15.0
S3	1	1.07	6.7
S4	0.5	0.54	3.5
S5	2	1.60	9.7
S6	1	1.05	6.6
S7	0.5	0.59	3.8
S8	5	3.00	16.8

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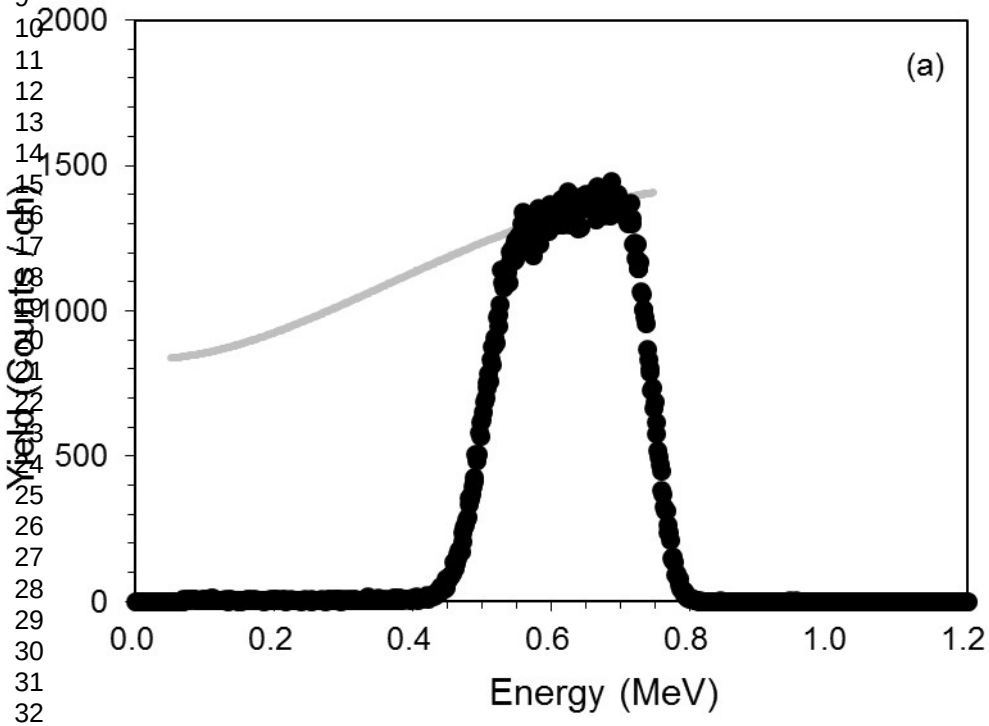


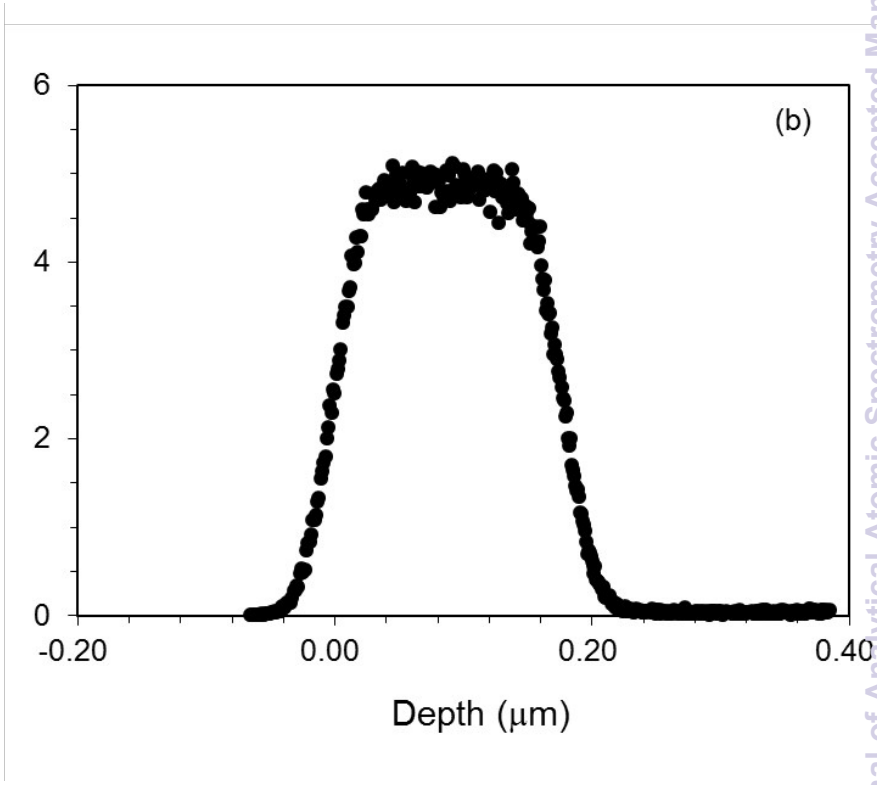
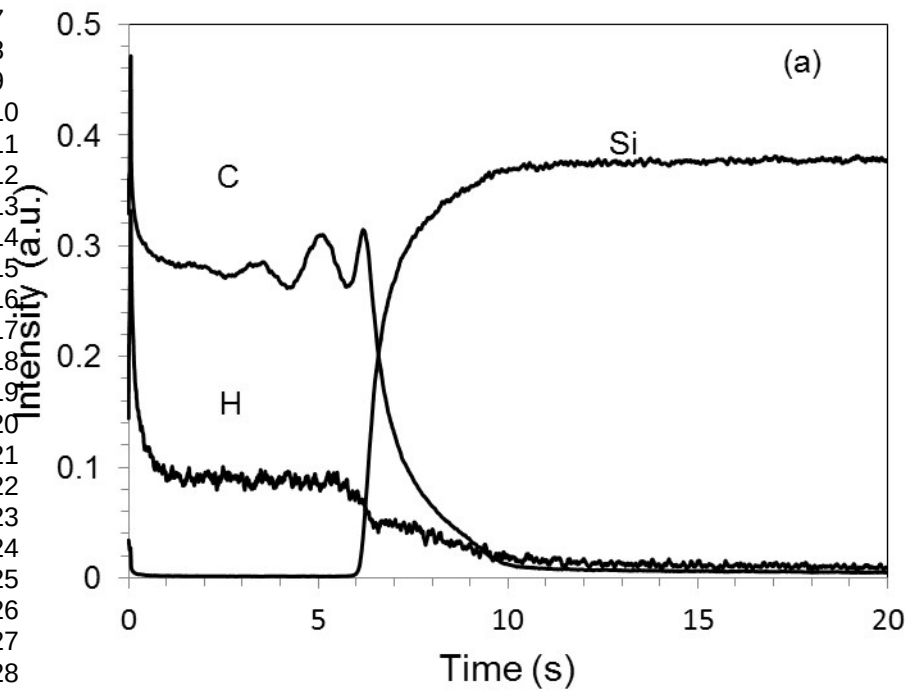


Fig1



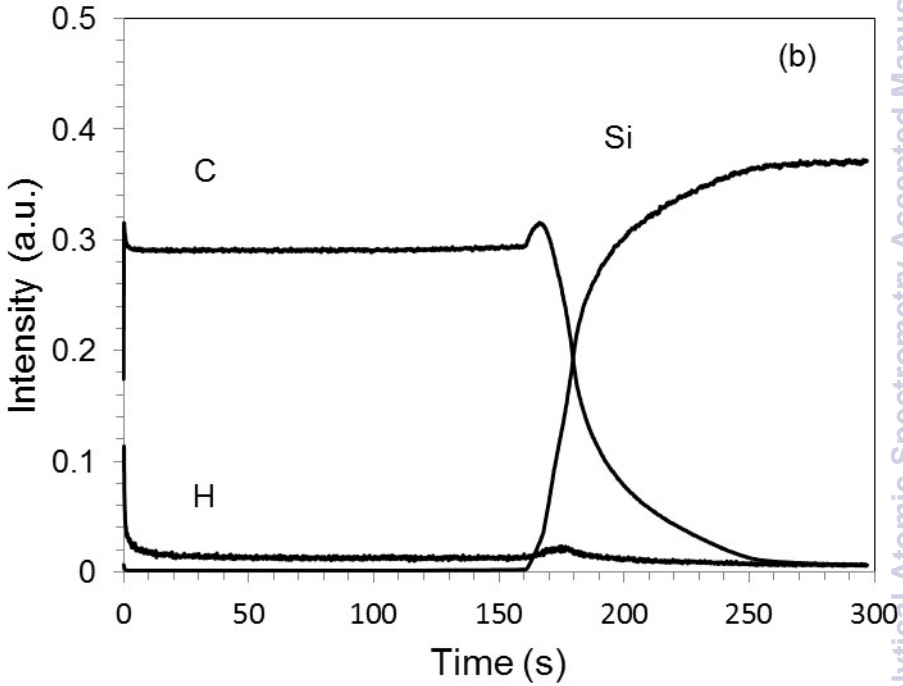


Fig2

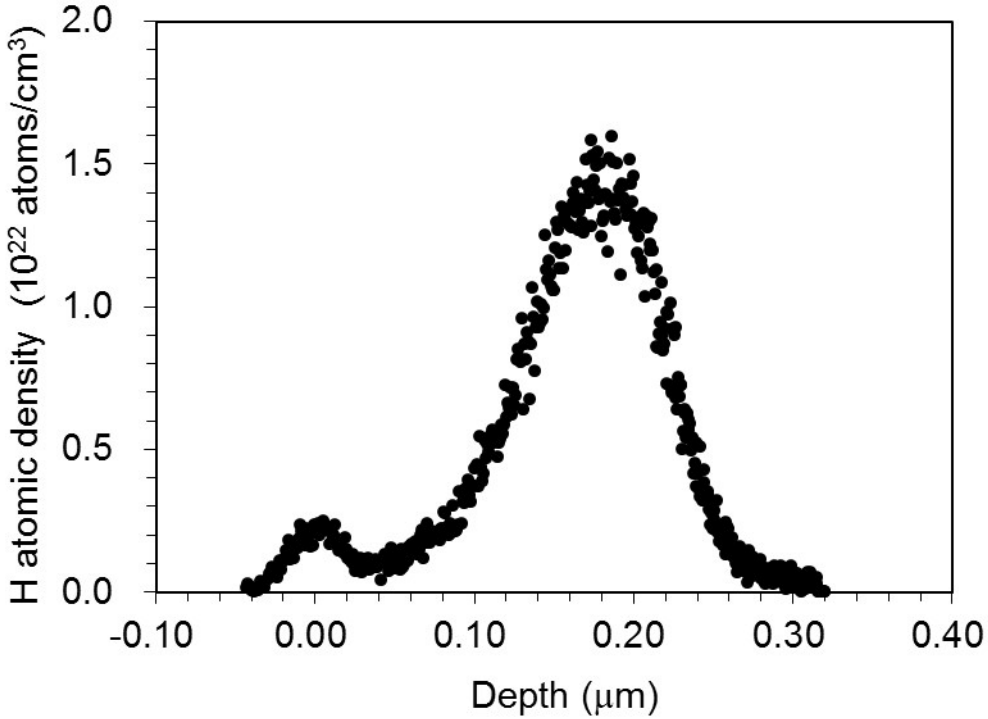


Fig3

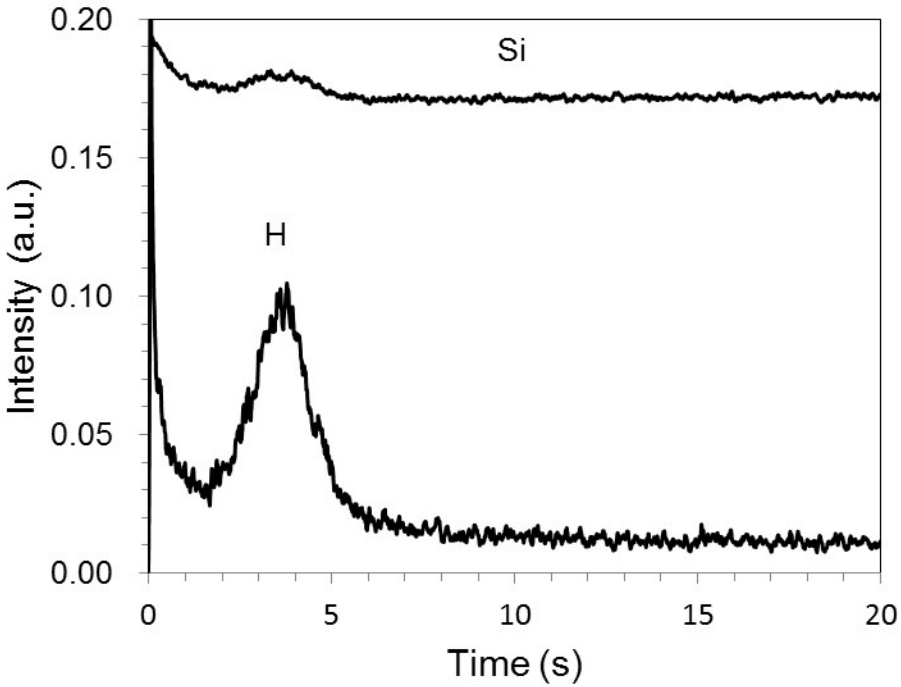


Fig4

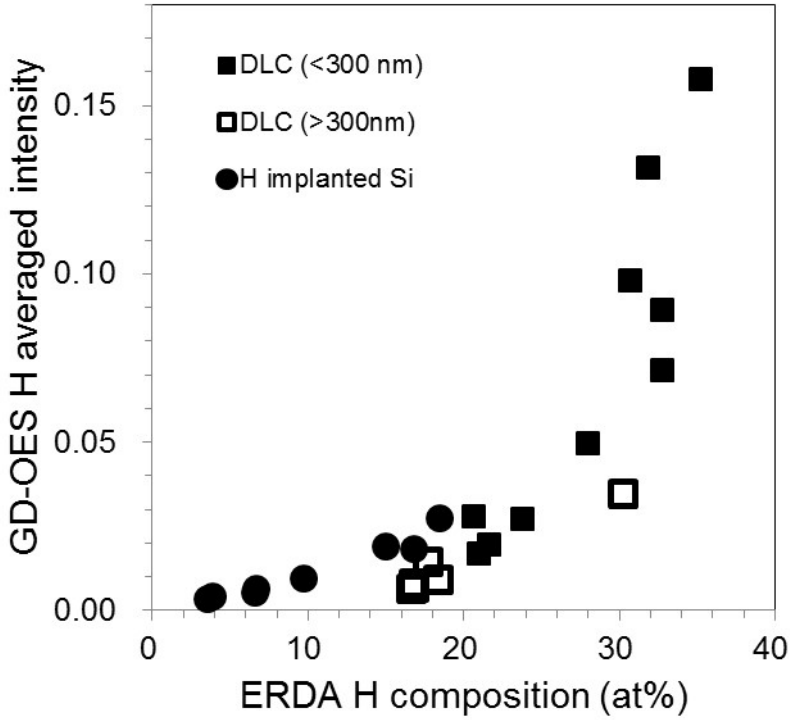


Fig5

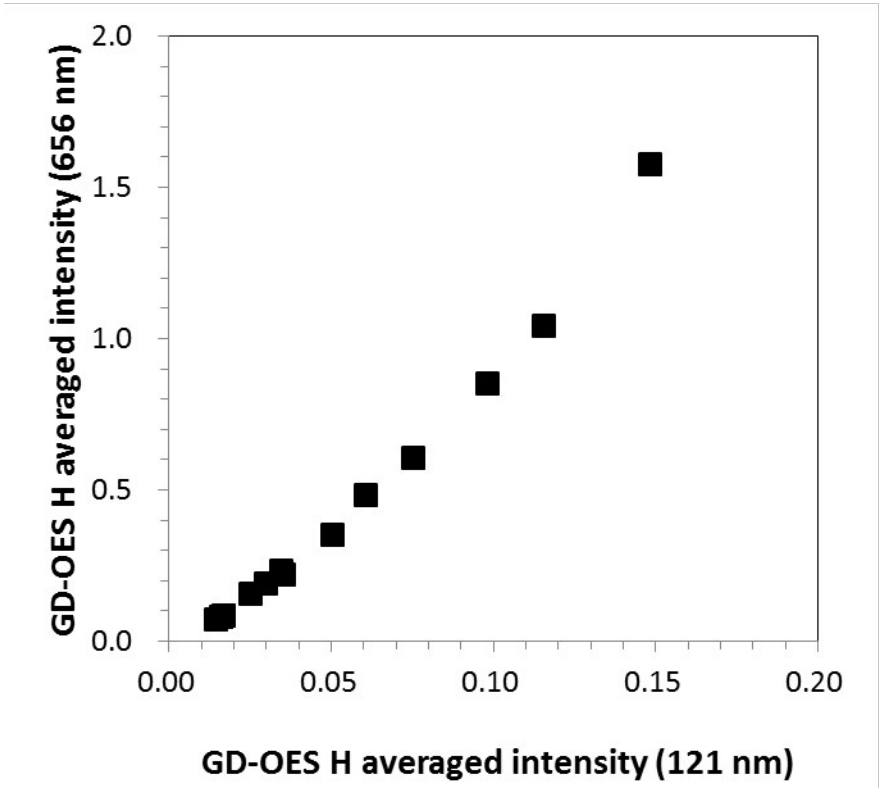


Fig6

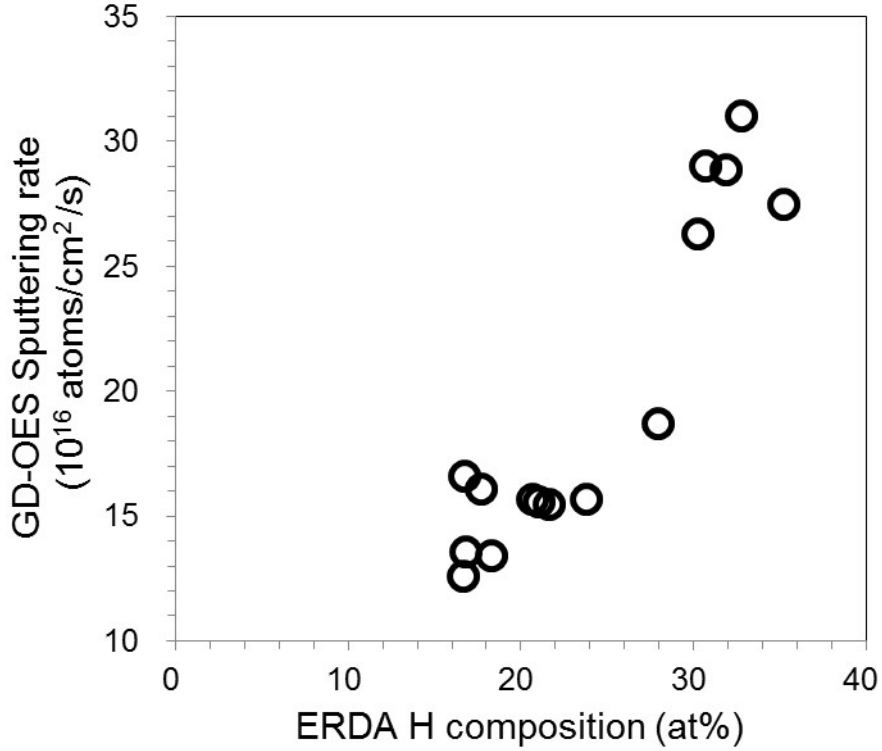


Fig7

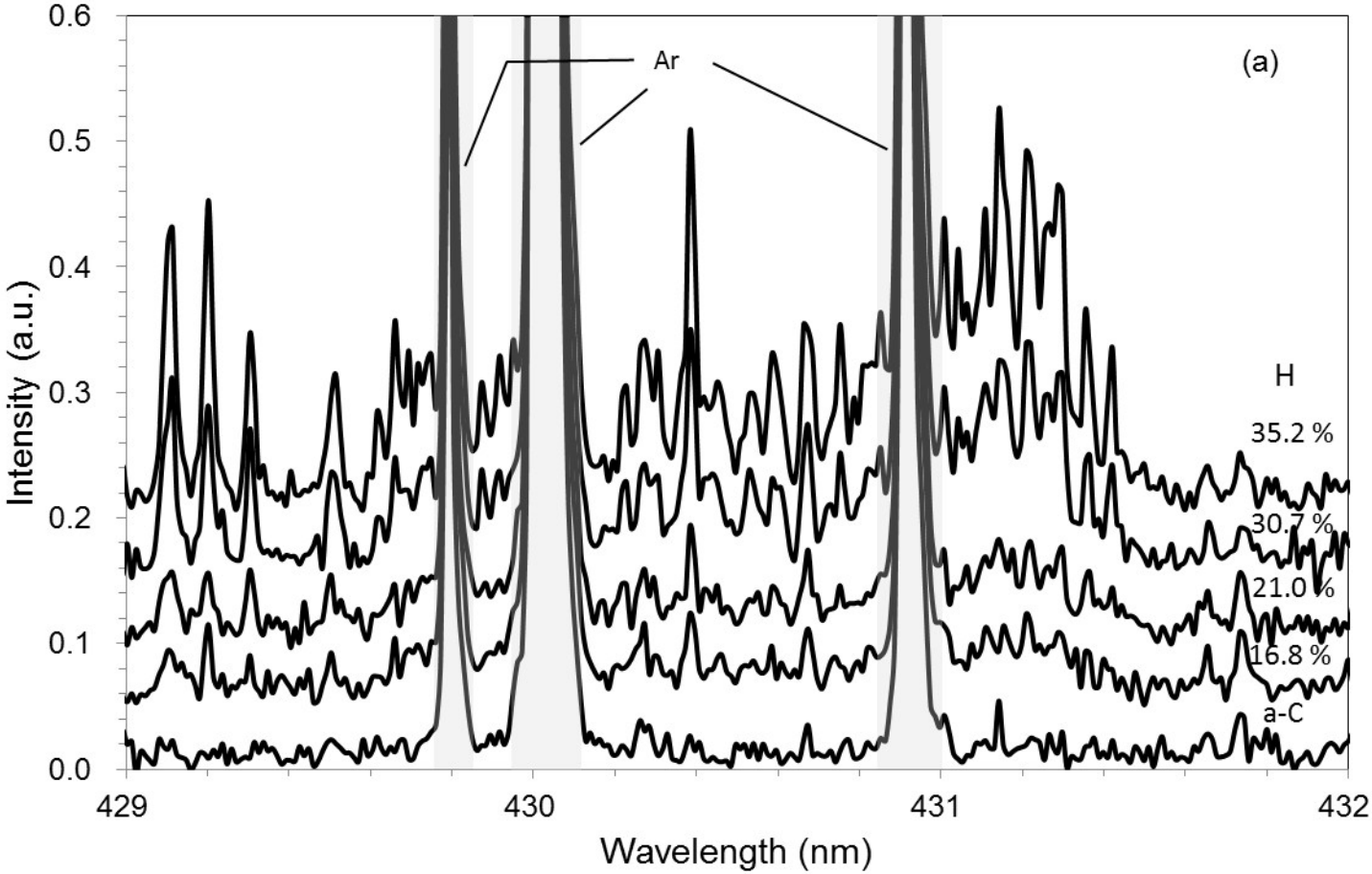
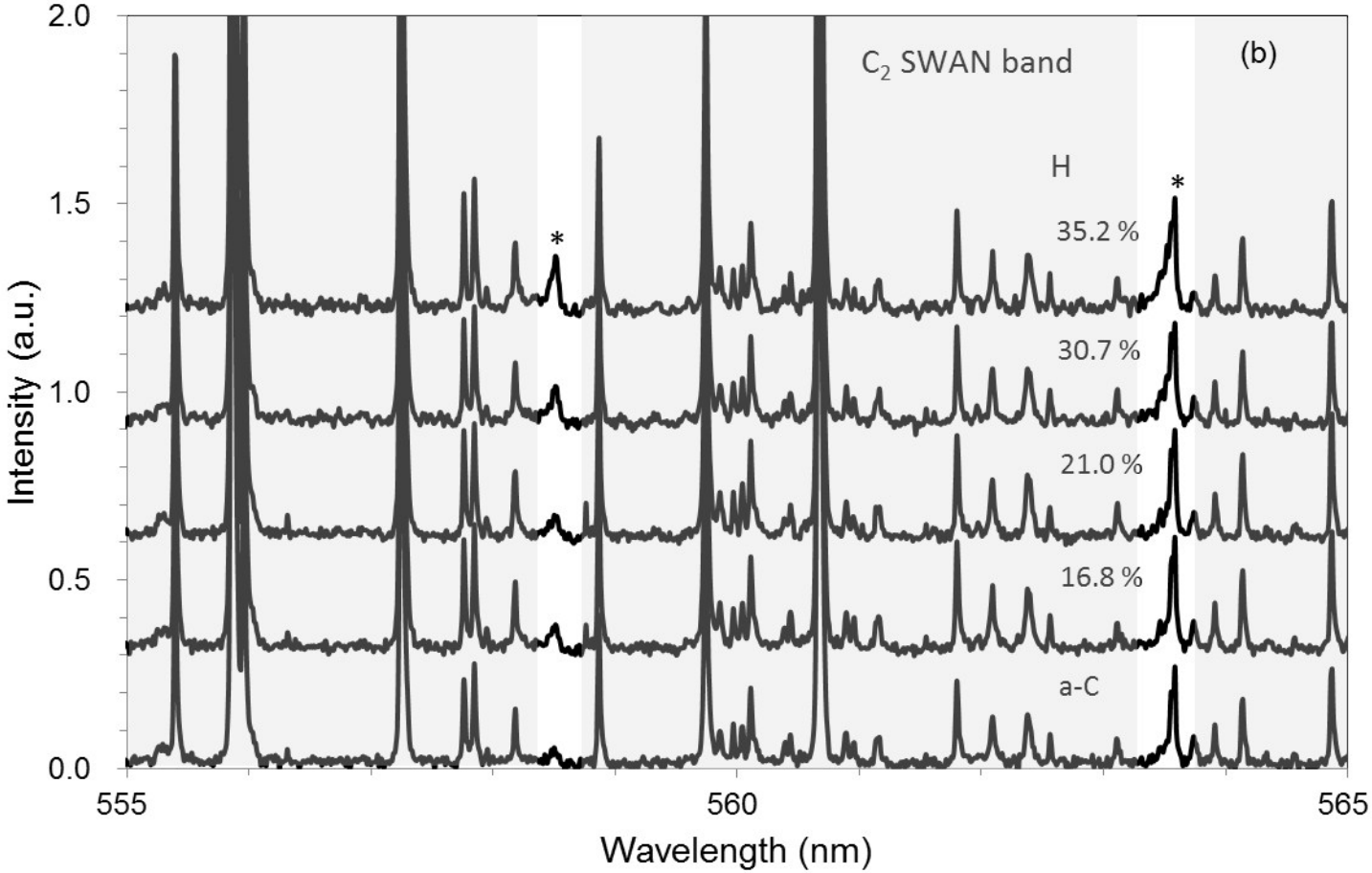


Fig8



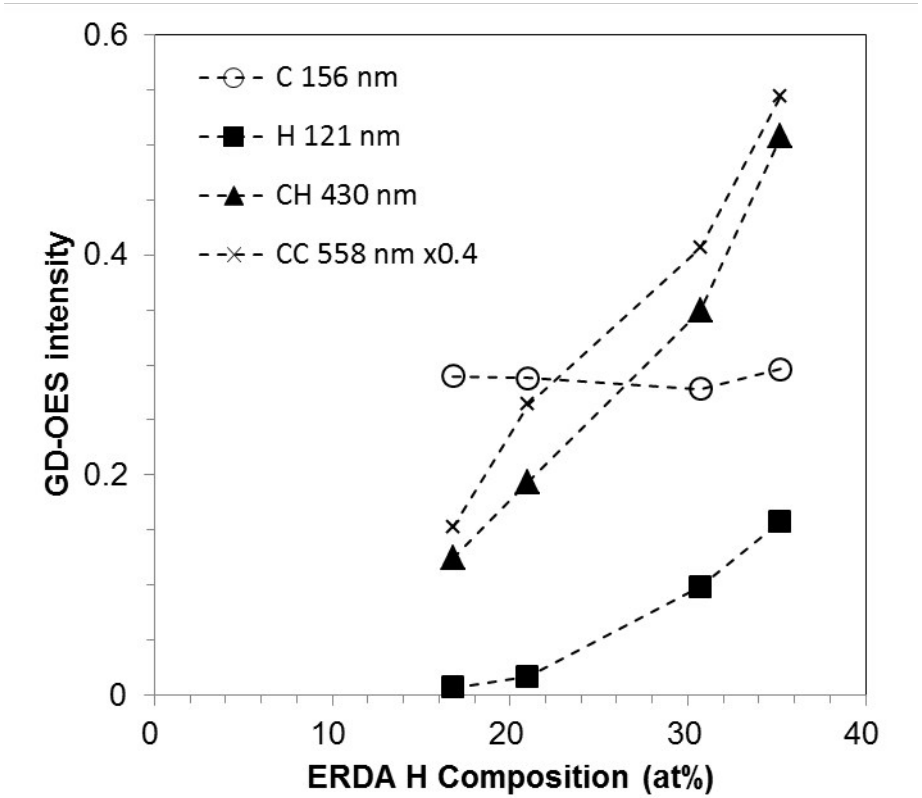


Fig9

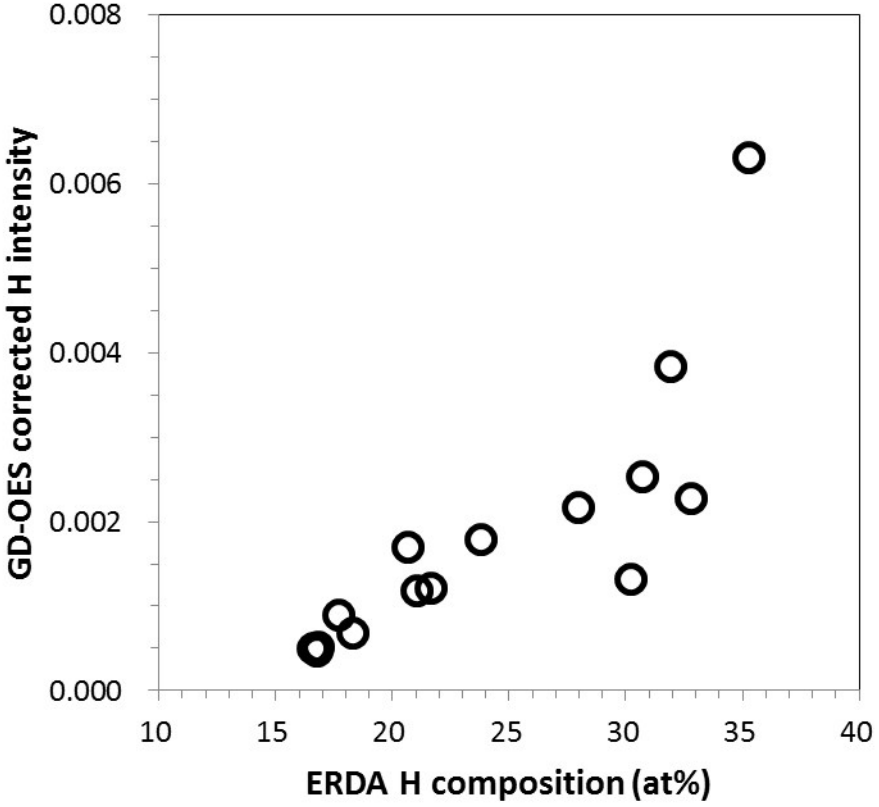


Fig10