Chemical analysis of $Cd_{1-x}Zn_xS$/CdTe solar cells by Plasma Profiling TOFMS

G. Kartopu[1,*], A. Tempez[2], A.J. Clayton[1], V. Barrioz[1], S.J.C. Irvine[1], C. Olivero[2], P. Chapon[2], S. Legendre[2], J. Cooper[3]

[1]Centre for Solar Energy Research (CSER), Glyndŵr University, OpTIC, St. Asaph Business Park, St. Asaph, LL17 0JD, UK

[2]HORIBA Jobin Yvon SAS, Avenue de la Vauve - Passage Jobin Yvon, 91120 Palaiseau, France

[3] HORIBA Scientific, HORIBA UK Ltd., Dalston Gardens, Stanmore, HA7 1BQ, UK

Thin film CdTe photovoltaic (PV) devices and reference layers obtained by the metalorganic chemical vapour deposition method have been studied for their chemical structure using plasma profiling time-of-flight-mass spectroscopy (PP-TOFMS, also called glow-discharge TOFMS). Different levels of arsenic (As) dopant in CdTe films were measured by PP-TOFMS and compared to results obtained from a more conventional depth profiling method (secondary ion mass spectrometry or SIMS). This comparison showed that PP-TOFMS has the sufficient sensitivity towards detection of the As dopant in CdTe and hence is suited as a rapid, low-vacuum tool in controlling the large scale production of CdTe PV materials.

Keywords: CdTe thin film PV; Glow-discharge; Plasma profiling (PP)-TOFMS; Depth profiling.

* Corresponding author. E-mail: giray.kartopu@glyndwr.ac.uk; Tel: +44-1745-535-213.

1. INTRODUCTION

Thin film CdTe based photovoltaic (PV) solar cells are amongst the most promising for solar electricity production worldwide. The current production cost of CdTe PV modules is well below $1/$W_p$[1] and hence can still compete with the recent surge of low-cost crystalline Si modules in the market. In order to maintain this competitiveness continuous efforts are needed to improve the conversion efficiency whilst maintaining/reducing the production cost. This may require the development of alternative fabrication methods for CdTe PV cells. To this effect, atmospheric-pressure metalorganic chemical vapour deposition (AP-MOCVD) is a promising method of fabrication since it offers more degrees of freedom than conventional processes with the doping and alloying of the active layers used in today's CdTe PV devices, ranging from the p-n junction-forming semiconductors, CdS and CdTe, transparent conducting oxide (TCO) to high resistivity metal oxide buffer layers.[2-4] Such control provides viable alternatives to, e.g., the customary approaches of window layer (CdS) thinning[5] and absorber layer (CdTe) (back surface) etching[6] which are often considered risky due to pinholes formation, often leading to micro-shorts.

The control and run-to-run reproducibility of the various dopant concentrations and their depth-profile within the aforementioned materials are key to the potential inline production of CdTe PV modules by the AP-MOCVD method. Even though conventional chemical analysis methods with high sensitivity such as Rutherford back scattering (RBS), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), etc. can successfully be used for this purpose, more rapid and cost-effective screening techniques could be highly advantageous for more frequent sampling which should allow tighter quality control, thereby reducing the associated material waste and costs.

Recently, low-vacuum operating glow discharge (GD) based techniques were applied to various PV materials, demonstrating their potential to replace the above-mentioned conventional depth profiling methods.[7,8] In this study, GD based techniques[9] optical emission spectrometry (OES) and plasma profiling time-of-flight-mass spectrometry (PP-TOFMS) were assessed to investigate the chemical structure of $Cd_{1-x}Zn_xS$/CdTe:As solar cells and the dopant concentration in CdTe:As thin films which were grown by AP-MOCVD.[2] The PP-TOFMS technique in particular combines fast erosion rates (few nm/s) with wide spectral (full mass coverage) detection. Furthermore, the recent capability of pulsing the RF excitation, found to be a key for profiling materials such as thin conductive layers on thick glass as developed for solar cells,[10] was also employed here to determine the dopant (As) concentration (C_{As}) in the CdTe absorber by PP-TOFMS. The pulsed RF mode reduces the thermal stress (induced by the plasma) and the sputtering rate (thereby enhancing the depth resolution) without compromise on sensitivity. The optimum level for As concentration in MOCVD CdTe:As solar cells was previously established to be about 2×10^{18} atoms/cm^3 for the bulk and $>2 \times 10^{19}$ atoms/cm^3 for the back surface (contact) layer.[11] Thus, the capability of accurately and rapidly determining such dopants in CdTe would be an important step towards establishing a screening method for the continuous (in-line) production of CdTe PV modules.

2. EXPERIMENTAL DETAILS

The CdTe devices were deposited using a horizontal AP-MOCVD reactor onto 7.5×5.0 cm^2 indium-tin-oxide (ITO)/boro-aluminosilicate superstrates (4-8 Ω sq. sheet resistance). The $Cd_{1-x}Zn_xS$ window layer was grown at 360 °C using ditertiarybutylsulphide, dimethylcadmium (DMCd) and diethylzinc (DEZn) organometallic precursors and hydrogen

carrier gas. Film composition was tuned by varying the (partial pressure) ratio of DEZn/DMCd. Then a bi-layer CdTe:As thin film structure was deposited comprising 2 μm thickness with ~10^{18} atoms/cm^3 As doping (*p*-CdTe) and 250 nm thickness with ~10^{19} atoms/cm^3 As doping (p^+-CdTe), resulting in a npp^+ device structure.[3,11] The precursors for As and Te were tris(dimethylamino)arsenic and diisopropyltelluride, respectively. Finally, $CdCl_2$ growth (using tertiary-butyl-chloride as the Cl source) and anneal treatments were achieved for cell activation as described previously.[12] A number of gold (Au) back contacts, each with 0.5×0.5 cm^2 area were then deposited onto the p^+-CdTe surface by thermal evaporation and defined the collection area for each device.

For reference, SIMS depth profiles were obtained to determine the concentration profiles of main elements of interest within the p-n junction, namely Cd, Te, As, S, Zn, and Cl, which were then used to compare the depth profiles obtained by GD methods. To assess the sensitivity of GD-OES and PP-TOFMS a number of CdTe:As layers were also deposited on CdS/boro-aluminosilicate substrates by varying the As precursor concentration.

SIMS was carried out on 1.0×1.0 cm^2 cut out samples at LSA Ltd. with a Cameca ims 4f instrument. The matrix element profiles were done using a positive ion (oxygen beam) rather than the negative ion (caesium beam) used for the As profiling since only a weak signal can be obtained from Cd as a negative ion. For the latter, a Cs^+ ion source with energy at 10 keV and current of 20 nA was used. The raster size was 100 μm analysing a sample area of 40 μm^2. Approximately 3.0×3.0 cm^2 samples were also characterised by OES and PP-TOFMS. A 13.56 MHz RF GD plasma fed with ultra-pure (99.9999%) Ar is used to remove material from the surface to the bulk and parallel excitation/ionisation of the sputtered species

combined with either an optical emission spectrometer or a mass spectrometer. When coupled to a high resolution optical system, the resulting technique is called RF GD-OES and is well established.[13] Such plasma source can also be combined with an orthogonal extraction TOFMS giving a technique called PP-TOFMS or GD-TOFMS. In this work, PP-TOFMS newly commercialized by Horiba Jobin Yvon was used. Furthermore, in the case of PP-TOFMS, the ultrafast detection allowed for monitoring the transient signals generated by the pulsed plasma. This unique time-resolved information is highly valuable as it allows for selecting the higher intensity time window ("RF-off" time also called afterglow), which permits to increase the sensitivity by a factor of up to 1000.[14,15]

The mass analyser is an orthogonal extraction time-of-flight tube best suited for monitoring fast transient signals. Ions are transferred from the plasma source operated at a few mbar to the mass analyser under 10^{-7} mbar through several interface stages. The interface region includes a notch filter used to attenuate the most intense ions that would lead to the microchannel plate detector saturation as well as electrostatic focusing and deflecting components. An important feature of this reflector based TOFMS is the high mass resolving power defined as $m/\Delta m$ (Δm being the half width at half maximum of Gaussian peak). In usual experimental conditions (for data shown here), the mass resolving power is ~3500 at mass m/z 208. In the data presented here, the RF generator sends a 2 ms long pulse of 40 W at a frequency of 250 Hz. The Ar pressure is regulated at 4 mbar. Within this 4 ms period 70 continuous spectra over mass range of interest (1-120amu) are acquired at a frequency of 32 kHz. Ar (m/z 40), Ar^{2+} (m/z 80), Cd (m/z 114), and Te (m/z 130) were attenuated by the notch filter. From these measurements a semi-quantification of elemental concentrations (usually in ppm) could be obtained via the Ion Beam Ratio (IBR)[15] analysis. However, to obtain exact quantification it is still necessary to use reference (calibration) samples.

3. RESULTS AND DISCUSSION

The normalized external quantum efficiency (EQE) spectra and a summary of the current density-voltage (*J-V*) data of two devices that were chemically studied are given in Fig. 1 and Table I, respectively. The device with the $Cd_{1-x}Zn_xS$ (CdZnS) window layer displays relatively higher photocurrents (and hence conversion efficiency) which correlated well with the improvement in device blue-response notable from the EQE spectra. This results from widening of the window layer bandgap (2.4 eV for undoped CdS) via $Cd_{1-x}Zn_xS$ alloy formation. The composition of the CdZnS window layer (prior to full device growth) was previously determined, via X-ray and optical spectroscopy, to be $Cd_{0.3}Zn_{0.7}S$.[2] The SIMS depth profiles of these devices are given in Fig. 2. Regions of window layer and absorber layers can be identified from the matrix element profiles (Fig. 2a and b), while bulk (CdTe:As) and back contact ($CdTe:As^+$) layer (BCL) can be understood from the (calibrated) As profiles (Fig. 2c), as indicated. Note also the presence and the high level of Zn content within the window layer of the CdZnS/CdTe device in Fig. 2b. In bulk CdTe, the C_{As} gradually increases towards the BCL for both devices which is consistent with long stabilisation time for the As flow. The higher open-circuit potential (V_{oc}) of the CdZnS/CdTe device (Table I) can partly be attributed to the relatively higher As concentrations observable in this device, as V_{oc} is correlated to the free carrier concentration.

Figure 3 shows the PP-TOFMS depth profile of selected elements obtained using pulsed RF mode for the same devices. (It must be said that GD-OES resulted in similar major element profiles but undetectable As signal and hence is excluded from this study altogether.) As opposed to SIMS, all element profiles could be obtained in a single TOFMS measurement. A sharp dip observable in most signals at the beginning of the measurements is due to the rapid

removal of surface contaminants (on sample and chamber surfaces) by the plasma. To increase sensitivity, the As signal was extracted from the afterglow region from 100 averaged RF source periods. It was notable that PP-TOFMS allows rapid screening of all the elements of interest within the solar cell structure (only selected elements shown in Fig. 3 for clarity).

The SIMS and PP-TOFMS profiles for a number of CdTe:As/CdS/glass samples with varying As concentration are given in Fig. 4a and b, respectively. For ease of monitoring, single As doping was adopted for each sample. All data are calibrated using the same CdTe:As implant sample as reference. The mean value for C_{As} is obtained by averaging data where the As signal is stable for all the spectra. For SIMS, this is between 200 and 700 nm from the surface as indicated by the two straight lines in Fig. 4a; for PP-TOFMS, the signal is useful from the surface up to the position indicated by the straight line at 1000 nm depth in Fig. 4b. The calibrated C_{As} (at %) values calculated from Figs. 4a and b are compared in Fig. 4c, to obtain a correlation between the two profiling methods. The agreement (curve fit) is reasonably good considering the very low concentration of As in the CdTe lattice (<0.1 at.%) for these films. Thus, it can be suggested that PP-TOFMS can be used reliably to determine As dopant concentration in CdTe.

4. CONCLUSION

CdTe:As thin films and high efficiency $Cd_{1-x}Zn_xS$/CdTe:As solar cells were deposited via the AP-MOCVD method and studied for their chemical structure using PP-TOFMS in comparison to SIMS. Measured chemical composition of two baseline CdTe solar cells suggested that the device performance (primarily V_{oc}) is dependent on the As concentration. Further, it is shown that PP-TOFMS has sufficient sensitivity and reliability in dopant (e.g.

As) profiling in such device structures and hence is suited as a rapid quality control tool in large scale production of CdTe PV modules.

Acknowledgement

The authors are grateful for financial support from the European Regional Development Fund (SPARC Cymru project), HEFCW funding for the Low Carbon Research Institute (LCRI), and Engineering and Physical Sciences Research Council UK (EP/K008633/1) are gratefully acknowledged.

References

[1] First Solar, http://www.firstsolar.com/Innovation/Advanced-Thin-Film-Modules

(retrieved on 15.01.2014).

[2] G. Kartopu, A.J. Clayton, W.S.M. Brooks, S.D. Hodgson, V. Barrioz, A. Maertens, D.A. Lamb, and S.J.C. Irvine, Effect of window layer composition in $Cd_{1-x}Zn_xS$/CdTe solar cells, Prog. Photovolt.: Res. and Appl., 2014, 22, 18-23.

[3] V. Barrioz, Y.Y. Proskuryakov, E.W. Jones, J.D. Major, S.J.C. Irvine, K. Durose, and D.A. Lamb, Highly arsenic doped CdTe layers for the back contacts of CdTe solar cells, Mat. Res. Soc. Symp. Proc., 2007, 1012, Y12-08.

[4] A.J. Clayton, S.J.C. Irvine, D.A. Lamb, W.S.M. Brooks, S. D. Hodgson, V. Barrioz, G. Kartopu, and S. Rugen-Hankey, Aluminium doped zinc oxide haze comparison for ultra-thin $Cd_{1-x}Zn_xS$/CdTe PV cells, Proceedings of PVSAT 9, Swansea, UK, April 2013, University of Swansea.

[5] T.L. Chu, S.S. Ferekides, C.Q. Wu, J. Britt, and C. Wang, 13.4% efficient thin-film CdS/CdTe solar cells, J. Appl. Phys., 1991, 70, (12), 7608-7612; M. Tsuji, T. Aramoto, H. Ohyama, T. Hibino, and K. Omura, Characterization of CdS thin-film in high efficient CdS/CdTe solar cells, Jap. J. Appl. Phys., 2000, 39, 3902-3906.

[6] K. Durose, P.R. Edwards, and D.P. Halliday, Material aspects of CdS/CdTe solar cells, J. Cryst. Growth, 1999, 197, 733-742.

[7] S. W. Schmitt, C. Venzago, B. Hoffmann, V. Sivakov, T. Hofmann, J. Michler, S. Christiansen, and G. Gamez, Glow discharge techniques in the chemical analysis of photovoltaic materials, Prog. Photovolt: Res. Appl., 2012, DOI: 10.1002/pip.2264;

[8] C. Gonzales-Gago, J. Pisonero, N. Bordel, A. Sanz-Medel, N. J. Tibbets, and V. S. Smentkowski, Radiofrequency pulsed glow discharge-ToFMS depth profiling of a CdTe solar cell: A comperative study versus time of flight secondary ion mass spectroscopy, J. Vac. Sci. Technol. A, 2013, 31(6), 06F106-1-7.

[9] I. S. Molchan, G. E. Thompson, P. Skeldon, N. Trigoulet, A. Tempez, and P. Chapon, Analysis of thin impurity doped layers in anodic alumina and anodic tantala films by glow discharge time-of-flight mass spectrometry, T. I. Met. Finish., 2010, 88, (3), 154-157.

[10] R. Aninat, G. Zoppi, A.Tempez, P. Chapon, N. S.Beattie, R.Miles, and I. Forbes, Crystallographic properties and elemental migration in two-stage prepared $CuIn_{1-x}Al_xSe_2$ thin films for photovoltaic applications, J. Alloys Compd., 2013, 566, 180-186.

[11] S.J.C. Irvine, V. Barrioz, D. Lamb, E.W. Jones, and R.L. Rowlands-Jones, MOCVD of thin film photovoltaic solar cells—Next-generation production technology?, J. Cryst. Growth, 2008, 310, 5198–5203.

[12] V. Barrioz, S. J. C. Irvine, E. W. Jones, R. L. Rowlands, and D. Lamb, *In situ* deposition of cadmium chloride films using MOCVD for CdTe solar cells, Thin Solid Films, 2007, 515, (15), 5808-5813.

[13] R. Payling, and T. Nelis, Glow Discharge Optical Emission Spectroscopy: A Practical Guide, (ed. N.W. Barneet), 2003, Cambridge, RSC Publishing.

[14] A. Tempez, N. Bordel, M. Hohl, L. Lobo, J.Orphal, C. Diplasu, A. Surmeian, M. Ganciu Petcu, and T. Nakamura, Ionization processes in a Grimm type source used in pulsed

r.f.-glow-discharge time-of- flight mass spectrometry, in: K. Tachibana (ed.), Proceedings of the 18th International Symposium on Plasma Chemistry (ISPC18), Kyoto, Japan, 2007, ISBN978-4-9903773-1-1, 267-271.

[15] L. Lobo, J. Pisonero, N. Bordel, R. Pereiro, A. Tempez, P. Chapon, J. Michler, M. Hohl, and A. Sanz-Medel, A comparison of non-pulsed radiofrequency and pulsed radiofrequency glow discharge orthogonal time-of-flight mass spectrometry for analytical purposes, J. Anal. At. Spectrom., 2009, 24, 1373-1381.

Tables.

Table I. Summary of *J-V* results (measured under AM1.5 illumination) for the CdTe devices characterised by depth-profiling methods.

	CdS/CdTe			**CdZnS/CdTe**		
	Best	**Ave.**	**σ =**	**Best**	**Ave.**	**σ =**
η (%)	**11.4**	**9.3**	**1.6**	**13.6**	**12.8**	**0.5**
J_{sc} (mA cm^{-2})	23.8	22.8	0.8	27.2	26.4	0.5
V_{oc} (mV)	**670**	**670**	**10**	**710**	**710**	**10**
FF (%)	73.3	60.8	9.3	72.1	68.7	3.2
R_s (Ω cm^2)	**2.1**	**2.1**	**0.3**	**2.5**	**2.3**	**0.3**
R_{sh} (Ω cm^2)	5917	3044	2500	12425	4620	3469

Figure Captions.

Fig. 1 Typical normalised EQE spectra of the CdS/CdTe and CdZnS/CdTe devices studied by SIMS and GD methods.

Fig. 2 SIMS depth profiles for the CdS/CdTe and CdZnS/CdTe devices reported in Fig. 1 and Table I: Matrix elements profiles for (a) CdS/CdTe, and (b) $Cd_{1-x}Zn_xS$/CdTe. (c) Comparison of the As concentrations within the bulk (CdTe:As) and BCL (CdTe:As^+) regions in these devices obtained in a separate SIMS run. The relatively higher V_{oc} observed for the CdZnS/CdTe device is attributed in part to the higher As concentrations in this device.

Fig. 3 PP-TOFMS depth profile of selected isotopes for the CdTe devices reported in Fig. 2: (a) CdS/CdTe, (b) CdZnS/CdTe. The As dopant profiles could also be obtained in these single measurements (compare to SIMS, which requires separate runs for As and matrix elements profiles, see Fig. 2).

Fig. 4 (a) SIMS and (b) PP-TOFMS depth profile for As in AP-MOCVD CdTe:As/CdS samples. (c) Comparison of C_{As} (at. %) values obtained from PP-TOFMS and SIMS methods.

Fig. 1

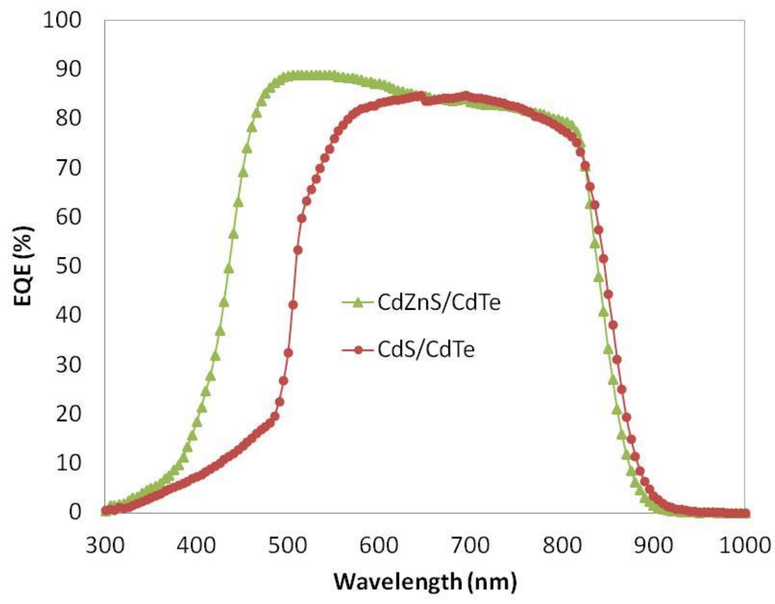

Fig. 2

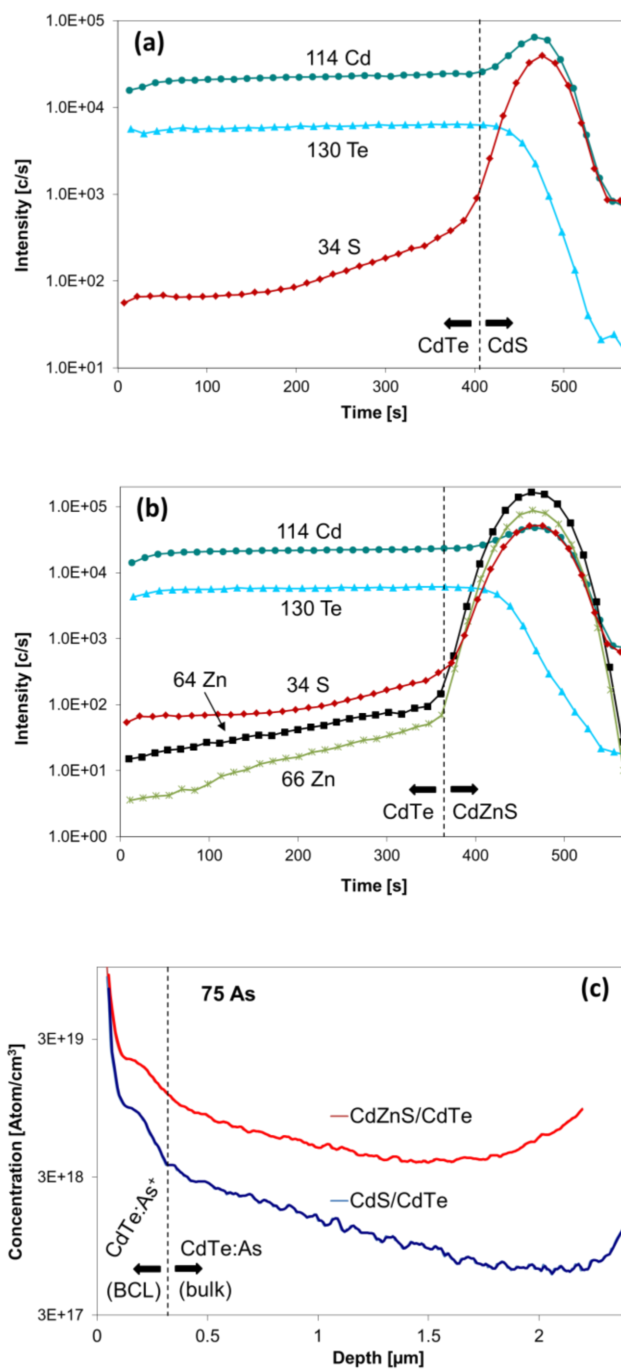

Fig. 3

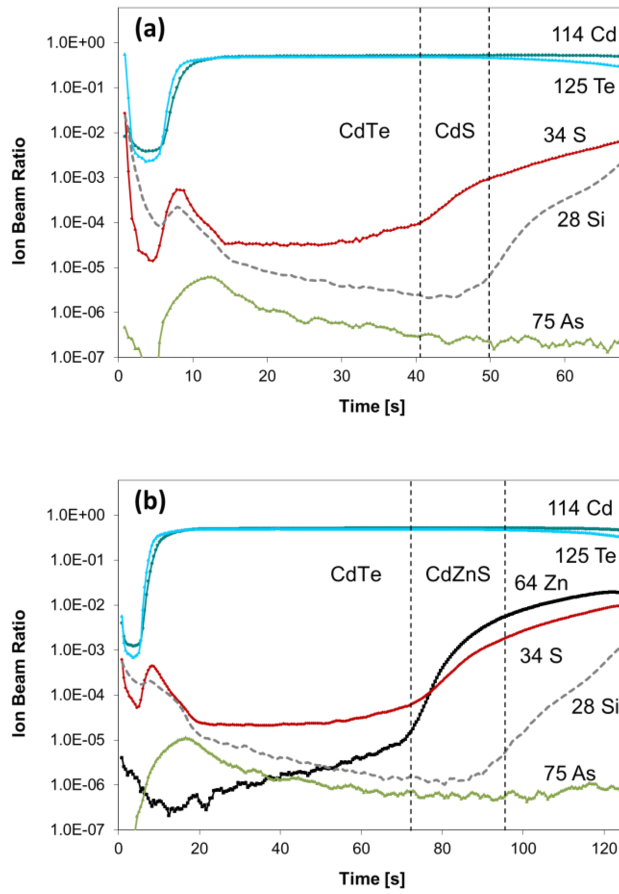

Fig. 4