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Oxygen-vacancy defects in electron-irradiated Si: the role of carbon in their behavior

C. A. Londos[1], E. N. Sgourou[1], A. Chroneos[2,3]

[1]*University of Athens, Solid State Physics Section, Panepistimiopolis Zografos, Athens 157 84, Greece*
[2]*Engineering and Innovation, The Open University, Milton Keynes MK7 6AA, United Kingdom*
[3]*Department of Materials, Imperial College London, London SW7 2AZ, UK*

Abstract

This is a detailed study of the effect of carbon impurity on the production of the oxygen – vacancy (VO) pair and its conversion to the VO_2 defect, in electron-irradiated Czochralski silicon (Cz-Si) material, by means of infrared spectroscopy. Upon irradiation vacancies are trapped by oxygen atoms to form VO pairs and it was determined that the presence of carbon enhances the production of this pair. This is attributed to the tendency of carbon to capture self-interstitials, thus decreasing the annihilation rate between vacancies and self-interstitials produced during the irradiation and therefore increasing the availability of vacancies to pair with oxygen atoms in the course of irradiation. Upon annealing a number of VO pairs are captured by oxygen atoms to form VO_2 defects. It was determined that the percentage of the VO converted to the VO_2 defects decreases as the concentration of carbon increases. The phenomenon is discussed in terms of the various reaction channels that VO pair participates upon annealing and how the presence of carbon impacts the balance between these reactions, affecting the final products of the involved processes. Finally, an opposite trend for the conversion of the VO_2 to the VO_3 defect was observed. The percentage of VO_2 converted to VO_3 is enhanced with the increase of carbon content. This finding is discussed in terms of the effect of carbon in the oxygen diffusivity and the final impact on the reaction $VO_2 + O_i \rightarrow VO_3$.

1 Introduction

Oxygen is the dominant impurity incorporated during processing in Czochralski grown Si and the oxygen-related defects have been investigated for decades [1-3]. Oxygen atoms, located at interstitial sites in the Si lattice (O_i), are the most effective sinks for the vacancies created in the course of irradiation leading to the formation of the *V*O pairs ($V + O_i \rightarrow VO$) the well-known A-centers. There are many technological and fundamental research reasons that demand a detailed understanding of the *V*O defect properties and behavior: Firstly, the defect introduces an acceptor level [4-6] in the forbidden energy gap at around E_c-0.17 eV. Due to its electrical activity the A-center acts as a recombination center [7,8], resulting in the deterioration of devices especially those operating in radiation environment, for instance Si detectors. Secondly, upon annealing *V*O interacts with oxygen impurities and vacancies leading to the formation [9] of various V_nO_m defects. Members of these families of defects cause [10] leakage currents in p-n junctions thus affecting negatively their properties. Thirdly, *V*O pair has been proposed [11,12] to act as a vehicle for oxygen aggregation processes in Si. Indeed, although the activation [13] energy for oxygen diffusion in Si is 2.53 eV, oxygen aggregation occurs with much lower activation energy [14] of 1.8 eV. To explain this, fast diffusing oxygen containing species are needed and the oxygen-vacancy pair was considered [12] as a potential candidate. Fourthly, on thermal processing of the Si material a number of *V*O pairs are captured by oxygen atoms to form VO_2 defects. The latter defect exhibits important properties, for instance the center appears to be bistable [15] and most importantly although VO_2 defect is electrically neutral, in its metastable configuration it manifests electrical activity. Precursor structures in the course of its final formation during the *V*O to the VO_2 conversion have also been reported [16]. More over it has been suggested that the VO_2 defect acts as nuclei for oxygen precipitation [17,18]. Aggregation and precipitation of oxygen are very important processes affecting the quality of Si-based

devices. Thus, any information on the formation of the VO defects and the mechanisms that govern its conversion to the VO_2 defect is considered very useful from the technological point of view, mainly for developing a fabrication process of Si-based devices with enhanced functionality. There is a fifth important reason: the formation and anneal of VO pair involves reactions with intrinsic defects (vacancies and self-interstitials) and this information can be used to control defect processes. To this end, the effect of other impurities, such as carbon present in the lattice on the behavior and properties of the VO and the VO_2 defects, is valuable.

Carbon is the second important impurity present in the lattice of as-grown Si [19-23]. It is an isovalent impurity in Si incorporated at substitutional sites in the lattice (C_s) and it readily traps self-interstitials produced in the course of irradiation. As a result, carbon atoms are injected at interstitial sites (C_i). Carbon interstitials exhibit in general a very interesting behavior [19,24-26], and being very mobile at room temperature they interact with primary defects and mainly with other C_s and O_i atoms to form the C_sC_i and C_iO_i defects, respectively. The latter defect is the most significant carbon-related defect and it is expected to impact the behavior of VO defect in carbon containing Cz-Si. It is therefore important to understand how carbon affects the mechanisms of formation of VO defect and its conversion to VO_2 defect.

Notably, the VO is optically active giving rise to an IR band at 830 cm^{-1} in the neutral charge state and an IR band at 885 cm^{-1} in the negative charge state [27,28]. Also, VO_2 defect gives an IR band at 888 cm^{-1}, although it is electrically inactive [27,29]. Therefore IR spectroscopy is a suitable tool to make proper investigation on the properties and behavior of the above oxygen – vacancy defects.

2 Experimental methods

We used samples cut from prepolished Czochralski Si wafers. Their corresponding carbon and oxygen concentrations are given in Table I. Three groups of samples were used, irradiated with 2 MeV electrons at three fluences: group one (samples labeled S1i, i = 1-4) with 5 x 10^{17} cm^{-2} , group two (samples labeled S2i, i = 1-3) with 1 x 10^{18} cm^{-2} and group three (samples labeled S3i, I = 1-2) with 2 x 10^{18} cm^{-2}, using the Dynamitron accelerator at Takasaki-JAERI (Japan). In the labels of the samples index i increases with the increase of the carbon content of the sample. The samples S12 and S13 are doped with Ge concentrations of 1 x 10^{17} and 1 x 10^{18} cm^{-3}, respectively. The sample S23 is doped with Sn concentration of 3 x 10^{17} cm^{-3}. These Ge and Sn concentrations have practically a negligible effect [30-32] on the production and evolution of *V*O defect and for the purpose of this work are simply considered as Cz-Si samples containing carbon.After the irradiation, all the samples were subjected to isochronal anneals up to 600 ^{o}C, in steps of $\Delta T \approx 10$ ^{o}C and $\Delta t = 20$ min. After each annealing step, the IR spectra were recorded at room temperature by means of a FTIR spectrometer with a resolution of 1 cm^{-1}. The two phonon background absorption was subtracted from each spectrum by using a float-zone sample of equal thickness.

3 Results and discussion

Fig. 1 presents the IR spectrum of a representative sample S22 among the group of samples used in this experiment. It shows the spectrum after irradiation and at characteristic temperatures in the course of the isochronal anneal sequence. The above annealing temperatures were purposely chosen to focus on the production and annealing of the main irradiation-induced defects of *V*O (830 cm^{-1}) and C_iO_i (862 cm^{-1}) and their products upon annealing that is the VO_2 (888 cm^{-1}), VO_3 (904, 968, 1000 cm^{-1}) and the C_sO_{2i} (1048 cm^{-1}) [19] defects. In the spectra weak bands also appear and these are attributed [19] to the C_iC_s

(546 cm^{-1}), C_sO_i (585, 637, 684 cm^{-1}) and the $C_iO_iSi_I$ (936, 1020 cm^{-1}) complexes. Another band [19] of C_iO_i at 739 cm^{-1} is also shown.

Fig. 2 shows the production of the *V*O defect as a function of the carbon concentration for the various irradiation fluences. Fig. 3 depicts how *V*O production varies with carbon content for each particular fluence used in the present study and in essence is an alternative representation of Fig. 2. As it is observed from Figs. 2 and 3 the concentration of *V*O defect increases with the increase of the carbon concentration. The relation is not linear, an indication that carbon affects indirectly the production of *V*O via the reactions taking place in the course of irradiation. Indeed, during irradiation *V* and Si_I are formed. Most of them are annihilated ($V + Si_I \rightarrow 0$). The remaining vacancies are captured by oxygen atoms to form *V*O defects. The presence of carbon has the following effect: Due to its strong tendency to trap Si_I, carbon competes with vacancies in their capture. This leads in a decrease in the rate of the annihilation reaction ($V + Si_I \rightarrow 0$), namely in an increase of the availability of vacancies to be captured by oxygen atoms. Thus the production of *V*O pairs increases, a fact verified experimentally (refer to Fig. 2). Additionally, it should be noted that in order to form a *V*O pair, a vacancy diffuses to an oxygen atom. It has been established experimentally that vacancies are mobile below room temperature. The onset of migration occurs [33] at ~70 K in *n*-type Si, at ~150 K in *p*-type Si and at ~200 K in high resistivity material with corresponding migration activation energies 0.18 eV for *n*-type, 0.32 eV for *p*-type and 0.45 eV for the high resistivity Si. These energies are much lower than that of 2.53 eV for oxygen diffusion [13]. The disappearance of vacancies upon annealing is accompanied in the spectra by the emergence of other signals, identified as vacancies trapped by other defects [34]. This clearly confirms [34] that the annealing occurs as a long range migration of vacancies. In this process a vacancy performs a number of jumps in the lattice until it encounters an oxygen atom. This is considered as a long-distance migration process in the course of which the

vacancy travels through the lattice where it may encounter self-interstitials. In the presence of carbon this possibility is substantially decreased and the possibility of the traveling vacancy to encounter and pair with an oxygen atom is enhanced. In Fig. 3 we observe that with the increase of fluence in the range of $5 \times 10^{17} - 2 \times 10^{18}$ cm^{-2} the concentration of *V*O increases as expected [35,36]. Notably, there were reports in the past [37] that variations of carbon content have no impact on *V*O formation in contrast with these studies. These observations can be attributed to the quality of the Cz-Si samples which ~50 years ago was inferior.

Upon thermal anneal the 830 cm^{-1} *V*O band begins to disappear from the spectra and another band at 888 cm^{-1} attributed to the VO_2 defect [27,29,38,39] begins to grow in the spectra. Fig. 4 shows the evolution of the *V*O and the VO_2 bands for the S22 sample. It also shows the evolution of the C_iO_i and C_sO_{2i} bands to be discussed later. Fig. 5 shows the conversion ratio of the a_{VO2}/a_{VO} versus carbon concentration for various fluencies. Fig. 6 is in essence an alternative representation of Fig. 5. It shows the conversion ratio of the a_{VO2}/a_{VO} for various carbon concentrations, for each particular fluence used in this study. As it is immediately seen from the latter figures, the conversion ratio a_{VO2}/a_{VO} decreases with the increase of the carbon concentration. To understand this behaviour one has to consider the main reactions that the *V*O participates upon annealing and how the formation of the VO_2 defect is affected by the presence of carbon. Three main processes have been suggested in the literature [1,24,27,38,39] to contribute in the demise of the *V*O pair upon annealing. The first is a fast process related with the destruction of A-centers by self-interstitials: $VO + Si_I \rightarrow O_i$ (1). The second is a slow process related with the migration of *V*O pair and its capture by immobile oxygen atoms to form the VO_2 defect. Indeed the decrease of the (830 cm^{-1}) IR band of *V*O in the spectra upon anneal above 300 ^oC is accompanied by the emergence of a band at (888 cm^{-1}) related [27] with the VO_2 defect $VO + O_i \rightarrow VO_2$ (2). However, annealing kinetics studies and comparisons of the concentration of the *V*O and the VO_2 defects has led

to the suggestion [27,29] that a third process should take place involving the capture of *V*O with some unknown sinks, or/and the reaction of *V*O by other defects and impurities: *V*O + X → *V*OX (3). It has been found [29] that X depends on the amount of carbon in Si material and it was suggested [29,39,40] that these unknown defects may be carbon related. Another relative suggested reaction is: *V*O + X → X′ + O_i (4). Also the following relative reactions have been considered [41] (*V*O + X → XO + *V*, *V*O + XO → XVO_2) (5). Furthermore, it deserves noting that reactions as *V*O dissociation (*V*O → *V* + O_i) (6), *V*O pairing with itself (*V*O + *V*O → V_2O_2, V_2O_2 → VO_2 + *V*) (7) and *V*O pairing with vacancies (*V*O + *V* → V_2O) (8) have also been considered and discussed in the literature [1,38,39]. It has been found [29] that more than half of the existed A-centers are not converted to VO_2 defects. The question about the lack of the *V*O pairs that are not transformed to VO_2 defects is still more or less unanswered and a complete picture about the fate of the loss *V*O pairs upon annealing has not been established so far. For instance, there are indications [40] that an electrical level E_c-0.20 eV and a Photoluminescence signal at 950-meV may be related with a defect formed upon annealing of the *V*O pair but this needs further verification. Also the hypothesis that the *V*O pair is missing due to its capture by some infrared inactive sinks needs further information to be verified. In this work in order to understand the influence of carbon in the conversion of *V*O to VO_2 we have firstly to take into account the reaction processes and especially those expressed by the relations (3), (4) and (5), indicating a direct or indirect role of carbon. For instance if X is carbon in reaction (3) then the formation of C*V*O defect is expected. Density functional theory (DFT) calculations indicate that the formation of the C_sVO defect is favourable (by -1.66 eV) [42]. This illustrates that the C_sVO defects are more bound as compared to the *V*O pairs (-1.32 eV). The DFT calculations also show that next nearest neighbor configurations of the C_sVO cluster are highly bound [42]. In essence when the *V*O pairs encounter a substitutional carbon atom at nearest neighbor or next nearest neighbor site,

they will be trapped and form the larger C_sVO cluster [42]. There are experimental reports [19] about the existence of a luminescence signal produced in irradiated Si, with a zero-phonon line at 488 meV (3942 cm^{-1}) correlated with a ($C_iO_i + V$) structure. The suggested [19] reaction scheme for the production of the center is: $C_s + Si_I \rightarrow C_i$, $C_i + O_i \rightarrow C_iO_i$, ($C_iO_i + V$) $\rightarrow$ 488 meV band and this defect anneals out at about 200 ^oC. These assignments are hypothetical and in view of the recent DFT evidence [42] it is possible to suggest an alternative reaction scheme ($VO + C_s \rightarrow C_sVO$) leading to the formation of the C_sVO defects. In this scheme the 200 ^oC annealing temperature reflects the binding energy difference (between the C_sVO and VO, i.e. -0.34 eV when considering nearest neighbor C_sVO defects) required to dissociate the VO defect from the C_s.

If X is a carbon-related defect, a potential candidate is the C_iO_i complex. Indeed, the reaction $VO + C_iO_i \rightarrow C_sO_{2i}$ has been reported previously [43]. The VO and C_iO_i bands anneal out together from the spectra at about 300 ^oC and a band at 1048 cm^{-1} has been correlated with the C_sO_{2i} defect. The whole process is depicted in Fig. 4. However, the annealing of the C_iO_i defect [24] occurs mainly by dissociation so that a small percentage is responsible for the VO loss in the course of annealing, as a consequence of reactions with carbon-related complexes. Thus other complementary reactions are taking place. In this line of thought the role of carbon in the reduction of the ratio a_{VO2}/a_{VO} could be mainly determined by the reaction $C_s + Si_I \rightarrow C_i$ and in particular its effect on the reaction $VO + O_i \rightarrow VO_2$. The following approach is envisaged. On thermal anneals and for temperatures above 300 ^oC, carbon may capture only temporarily the self-interstitials. In essence, at these temperature carbon interstitials only temporarily form and then carbon atoms return back to substitutional sites releasing these self-interstitials ($C_i \rightarrow C_s + Si_I$). A percentage of these self-interstitials then reacts with VO_2 defects. In this sense, with the increase of carbon, the number of VO_2 defects formed decreases. It is possible that some of the C_i's could react with O_i atoms to

form C_iO_i pairs, something consistent with the slight increase of the latter defect prior to annealing that is in the temperature range 250-300 ^oC. Of course at these temperatures most of the C_i return at substitutional sites liberating Si_I's, which react with VO_2 defects as mentioned above. One may also consider that some of these self-interstitials react with VO defects ($VO + Si_I \rightarrow O_i$), besides those reacting with VO_2 defects. Thus, the number of VO pairs available to be converted to VO_2 defects becomes also smaller. We argue that there is a balance between these two processes so that on the whole the presence of carbon leads to less VO_2 defects in relation with the initial VO defects. In other words, less VO are converted to VO_2 in the course of annealing, when carbon is present. This is equivalent with saying the ratio a_{VO2}/a_{VO} decreases with the increase of the carbon concentration. In this framework it deserves mentioning that a defect reaction of VO_2 defect with C_i has been suggested [44] to occur in high temperature (600-800 K) electron irradiations according to the reaction (VO_2 + $C_i \rightarrow C_iVO_2$ or C_sO_{2i}). Again in view of the recent DFT evidence [42] it is possible to suggest alternative reaction schemes ($VO_2 + C_s \rightarrow C_sVO_2$ or $O_i + C_sVO \rightarrow C_sVO_2$) leading to the formation of the C_sVO_2 defects. The possibility of the existence of these extended clusters needs to be investigated further.

To explain the effect of carbon on the production of VO defect and its conversion to VO_2 defect we have suggested a different role for carbon in the two cases. In the production process carbon traps self-interstitials thus suppressing the annihilation ratio with vacancies, which lead to an increase of the available vacancies leading to an enhancement of VO productivity. However, in the annealing process of VO and its conversion to the VO_2 defect, carbon act as temporary trap for the self-interstitials which upon releasing they destroy some of the VO_2 defects leading finally to a reduction of VO_2 defects, alternatively to a diminishing of the a_{VO2}/a_{VO} ratio. Thus, both processes, namely the production of VO defect and its

conversion to the VO_2 defect are limited by reactions with self-interstitials the availability of which and their role is determined by the presence of carbon impurity.

Fig. 7 shows the conversion ratio of the a_{VO3}/a_{VO2} versus carbon concentration for various fluencies. Fig. 8 is in essence an alternative representation of Fig. 7. It shows the conversion ratio of the a_{VO3} /a_{VO2} for various carbon concentrations, for each particular fluence used in this study. It is observed that this conversion ratio between VO_2 and VO_3 defects decreases with the increase of the carbon concentration as opposed to the case between the VO_2 and VO_3 defects. Notably however, in the occasion of the VO_3 defect its formation occurs at temperatures above 450 ^oC through the reaction $VO_2 + O_i \rightarrow VO_3$. At these temperatures oxygen impurity is already mobile [1], able to diffuse in the lattice and meet with the VO_2 defect. In other words, in the case of the VO_3 formation both partners that is VO_2 defect [24] and oxygen atoms are moving in the lattice attaching each other in a $VO_2 + O_i$ structure. Observations of an enhancement of oxygen diffusion in carbon containing Cz-Si, subjected to heat treatments at ~750 ^oC, has been attributed [45] to the formation of fast diffusing oxygen –carbon molecules. We can extend this idea in the case of irradiated Si and for anneals above 450 ^oC. In particular we envisage the formation and rapid dissociation of oxygen –carbon complexes, a process which promotes in essence the diffusion of the oxygen impurity in the lattice. More specifically, it has been suggested [1] that large clusters formed as a result of the irradiation can release self-interstitials with the increase of temperature. In that case carbon interstitials form ($C_s + Si_I \rightarrow C_i$), which are very mobile and they are captured by oxygen interstitials atoms to form C_iO_i defects. Above 450 ^oC these defects are unstable and they dissociate almost immediately only for the carbon atom to be trapped again by oxygen atom and then detrapping and so on. In other words, these oxygen-carbon complexes act as transient species and by their sequential formation and dissociation, in a self-sustaining loop at these temperatures, they could enhance the oxygen diffusion. Notably,

a similar behavior has been suggested [46] by the interaction of oxygen atoms with intrinsic defects. In this case the formation of oxygen-vacancy transient pairs could enhance oxygen diffusivity as well. Going one step forward in our picture, the enhanced oxygen diffusivity due to the presence of carbon could result in an increase of the probability of encountering VO_2 defects with O_i atoms, as can be inferred by simple reaction kinetics arguments, leading finally to an increase of the total number of the formed VO_3 defects, that is to an enhancement of the a_{VO3} / a_{VO2} ratio.

Interestingly, the role of carbon on the sequential formation of VO_n defects is different, depending on the temperature that determines the particular conversion. In the case of VO_2 formation carbon affects reactions with self-interstitials although in the case of VO_3 defects we have considered the likelihood of the formation of transient species involving carbon in their structures to understand the experimental observations. The present study is part of a concerted effort by the community to understand the impact of isovalent doping and/or localized strain on the defect processes of semiconductors [47-49].

4 Conclusions

We have investigated the effect of carbon on the properties of VO defect in electron-irradiated Cz-Si. In particular, we have focused our studies on the effect of carbon on the production VO defect and on its conversion to the VO_2 defect, upon thermal annealing. It was found that when carbon concentration increases the production of VO defect is enhanced although its conversion to the VO_2 defect is suppressed. The phenomena were attributed to the ability of carbon to trap self-interstitials thus affecting the balance among the reactions that govern the VO production and its conversion to the VO_2 defect. Additionally, the a_{VO3} / a_{VO2} ratio increases with the increase of the carbon content as a result of the enhanced effect of carbon on the oxygen diffusivity of Si.

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Table I The concentration of *V*O and the ratio a_{VO2}/a_{VO} and a_{VO3}/a_{VO2} for the used samples irradiated with 2MeV electrons at various fluences.

Sample New name	Sample Old name	$[C_s]_o$ 10^{16} (cm^{-3})	$[C_s]_{a.i.}$ 10^{16} (cm^{-3})	$[O_i]_o$ 10^{17} (cm^{-3})	$[O_i]_{a.i.}$ 10^{17} (cm^{-3})	Fluence (e cm^2)	[VO] 10^{16}	a_{VO2}/a_{VO}	a_{VO3}/a_{VO2}
S11	E4	<1	-	9.6	9.2	$5x10^{17}$	2.3	0.83	0.4
S12	Ge1	2	<2	9.6	9.05	$5x10^{17}$	3.4	0.63	0.44
S13	Ge3	3	2	10	9.42	$5x10^{17}$	3.5	0.62	0.48
S14	E3	16	9.6	10.2	9.8	$5x10^{17}$	3.9	0.56	0.54
S21	M4	5	<2	9.5	9.04	$1x10^{18}$	5.87	0.48	0.43
S22	H3	22	13.2	9.3	9	$1x10^{18}$	6.2	0.41	0.46
S23	Sn3.1	47	18	9.6	8.5	$1x10^{18}$	7.3	0.38	0.58
S31	M7	4	2.3	10.5	9.72	$2x10^{18}$	7.2	0.55	0.33
S32	M5	8.8	3.85	9.45	8.69	$2x10^{18}$	9.8	0.33	0.44

Figure captions

Fig. 1.IR spectra of the S22 sample after irradiation and at 250, 400 and 500 ^{o}C in the course of anneals.

Fig. 2 The production of *V*O defect as a function of carbon concentration for the various fluences.

Fig. 3 The production of *V*O defect for the various carbon concentrations of the samples, for each particular fluence used in this work.

Fig. 4 Evolution of the IR bands of *V*O (830 cm^{-1}), C_iO_i (862 cm^{-1}), VO_2 (888 cm^{-1}) and C_sO_{2i} (1048 cm^{-3}) defects in the (2 MeV / 1x10^{18} cm^{-2}) electron-irradiated S22 sample upon isochronal annealing.

Fig. 5 The conversion ratio a_{VO2}/a_{VO} as a function carbon concentration for the various fluences.

Fig. 6 The conversion ratio a_{VO2}/a_{VO} for the various carbon concentrations, for each particular fluence used in this work.

Fig. 7 The conversion ratio a_{VO3}/a_{VO2} as a function carbon concentration for the various fluences.

Fig. 8 The conversion ratio a_{VO3}/a_{VO2} for the various carbon concentrations, for each particular fluence used in this work.

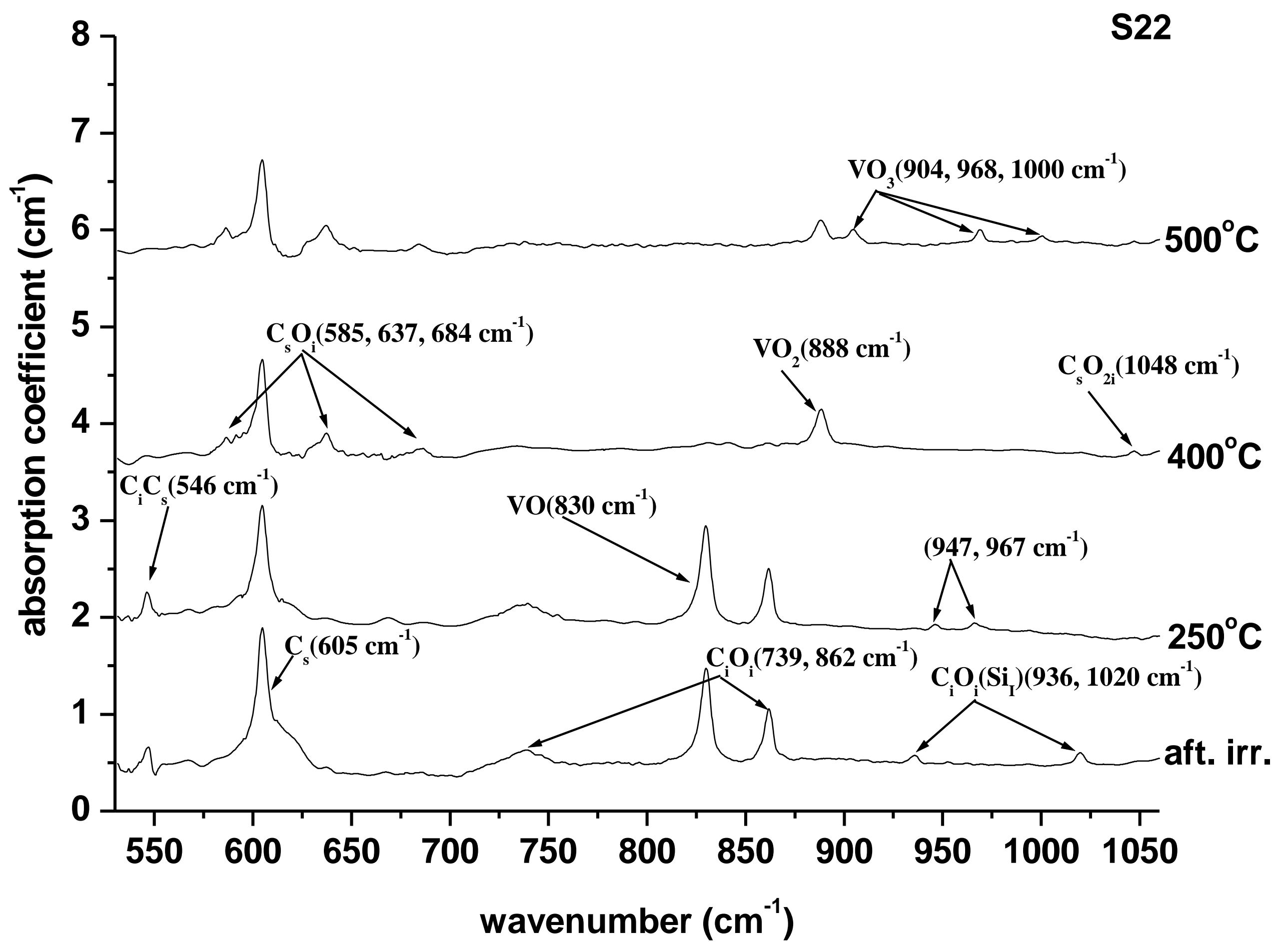

Fig.1

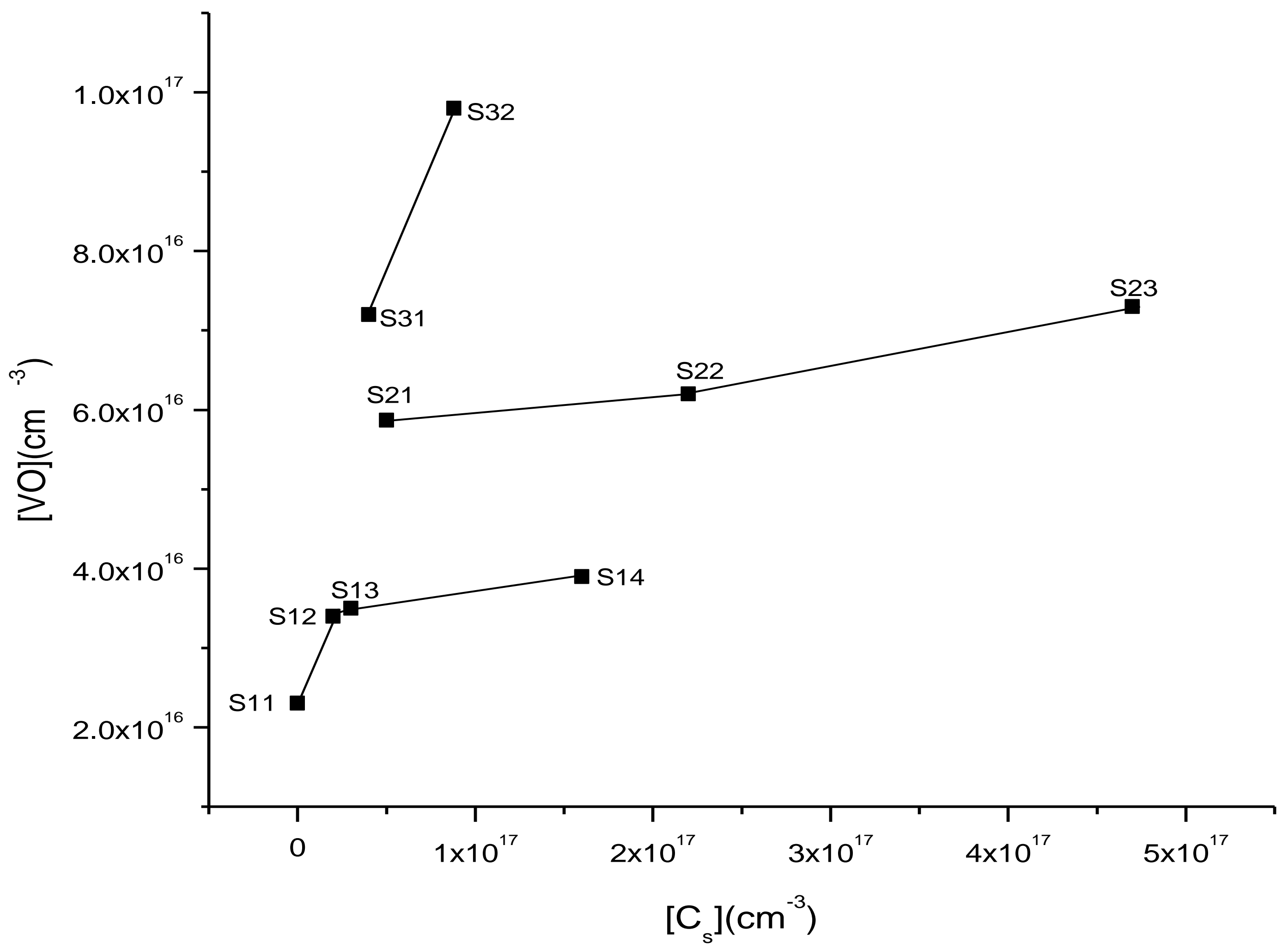

Fig.2

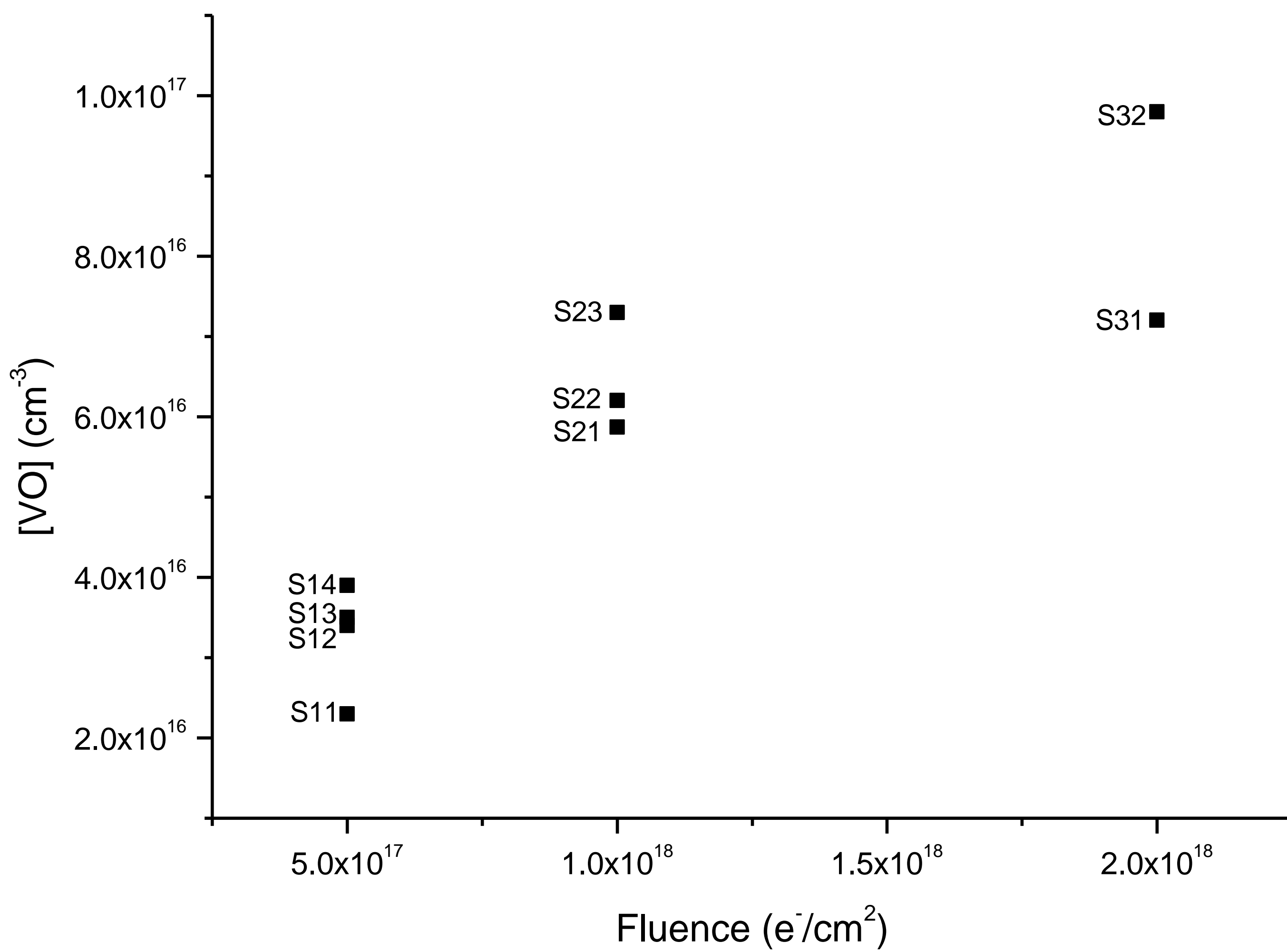

Fig. 3

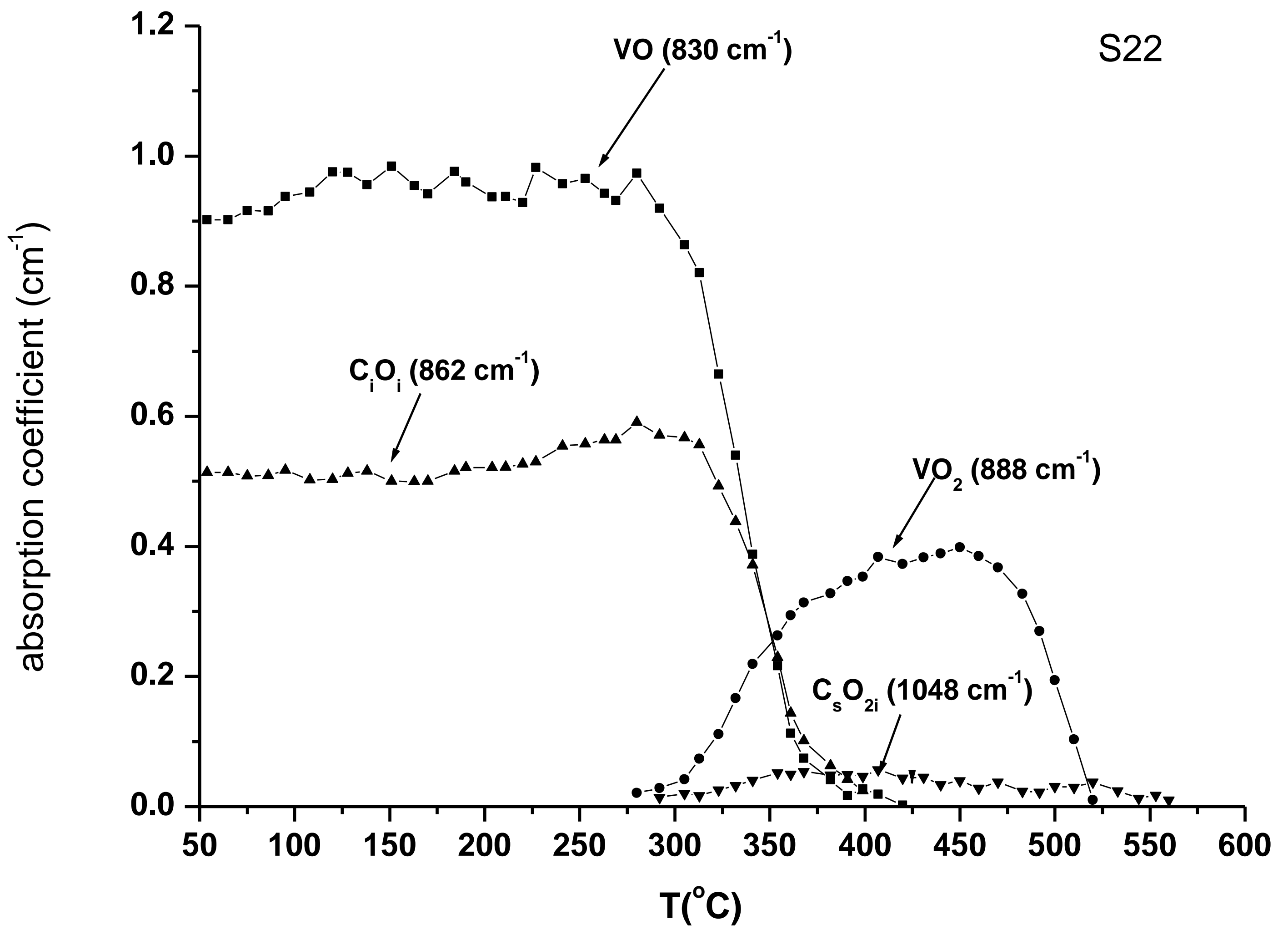

Fig.4

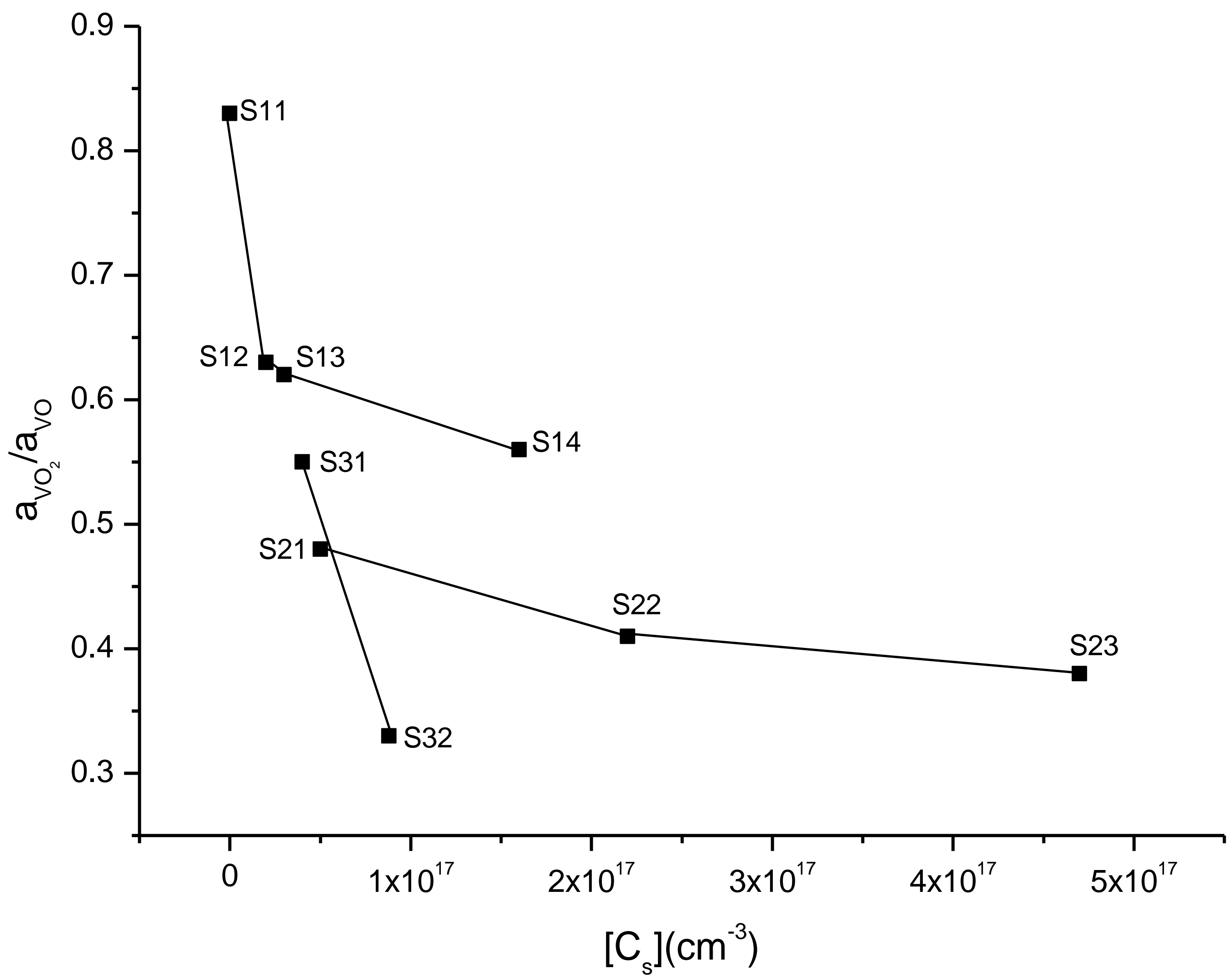

Fig.5

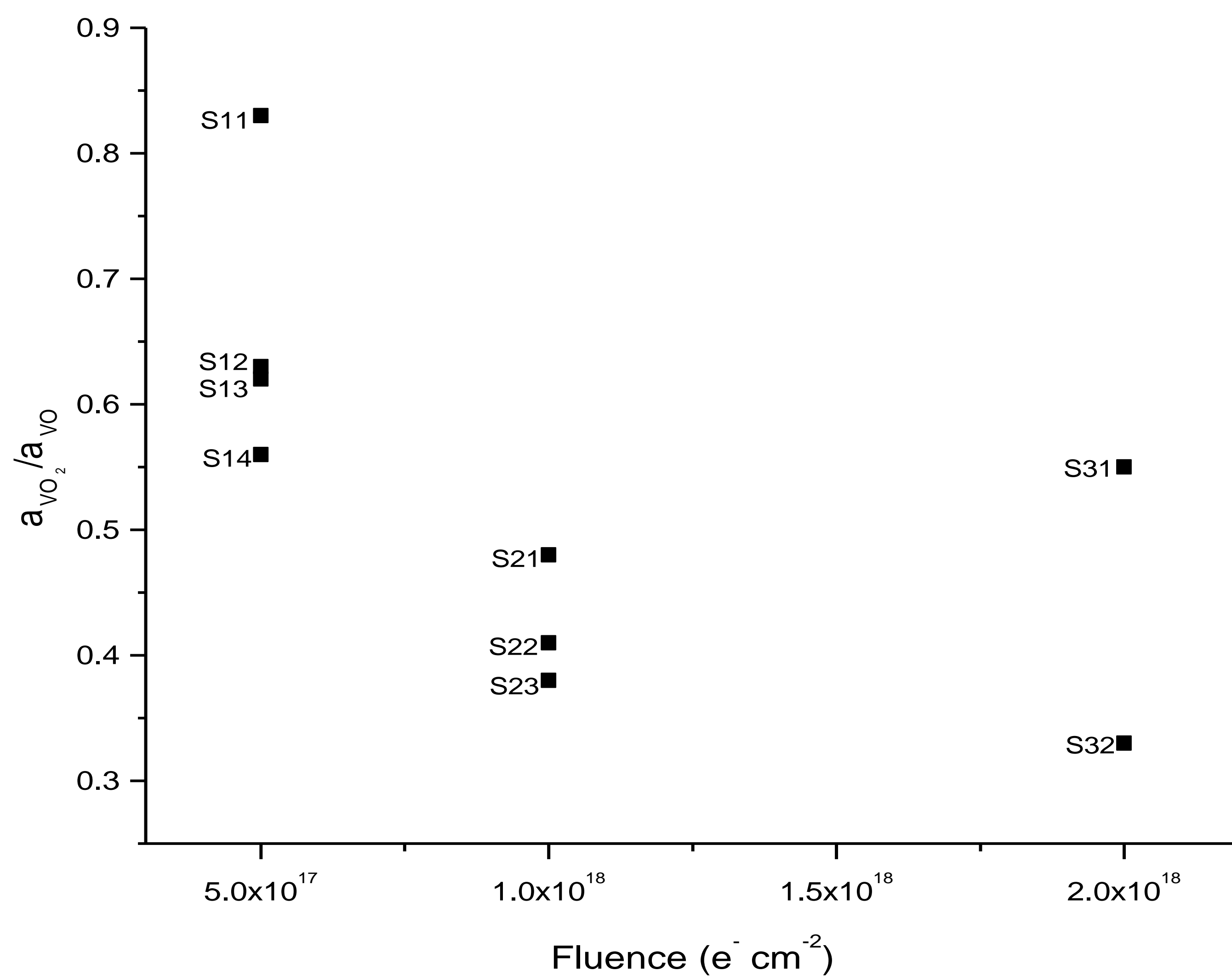

Fig. 6

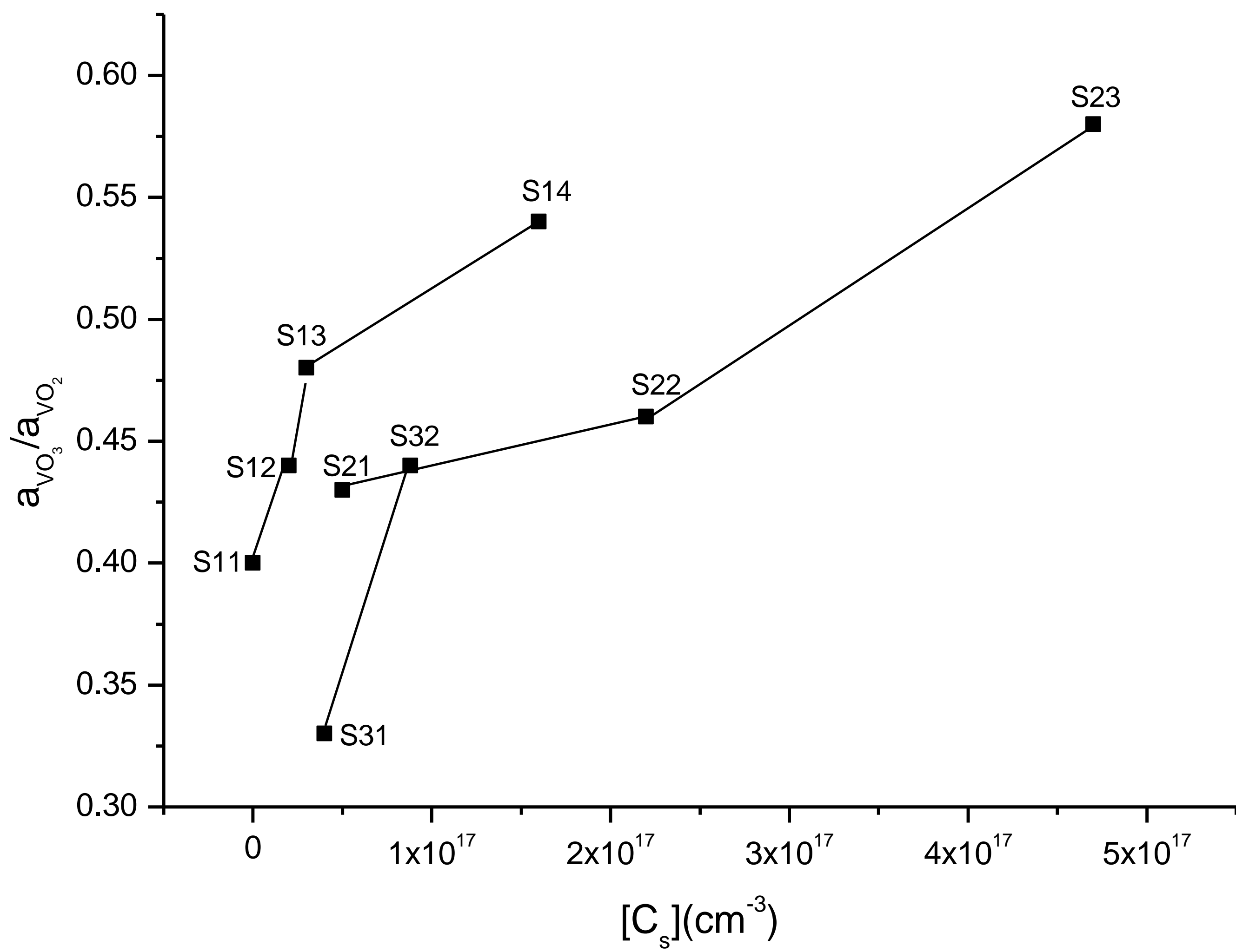

Fig.7

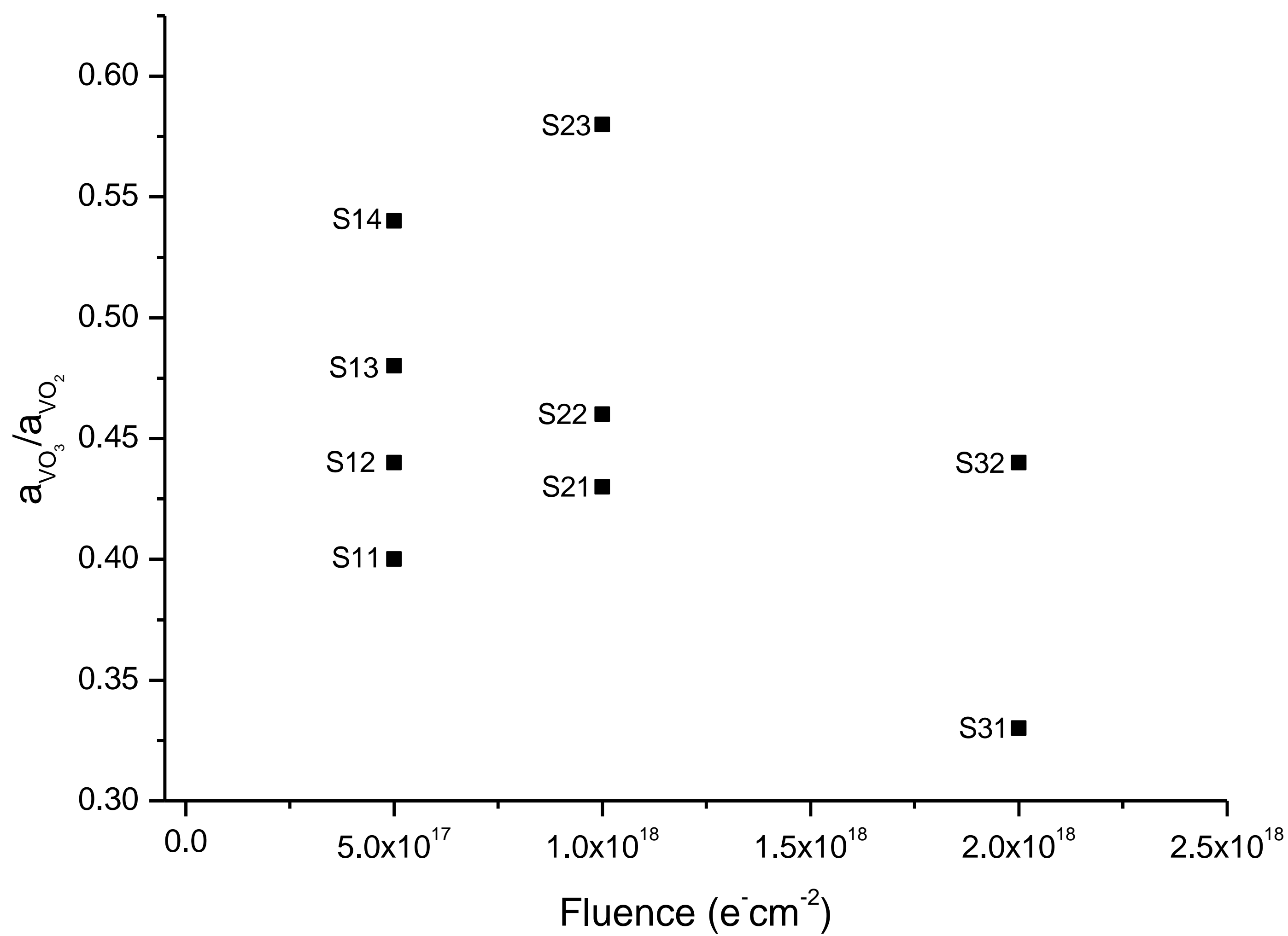

Fig. 8