Oxygen vacancy and $E_C - 1$ eV electron trap in ZnO

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Abstract

Fourier transform deep level transient spectroscopy has been performed between 80 and 550 K in five $n$-type ZnO samples grown by different techniques. The capture cross section and ionization energy of four electron traps have been deduced from Arrhenius diagrams. A trap 1 eV below the conduction band edge is systematically observed in the five samples with a large apparent capture cross section for electrons ($1.6 \pm 0.4 \times 10^{-13}$ cm$^2$) indicating a donor character. The assignment of this deep level to the oxygen vacancy is discussed on the basis of available theoretical predictions.

Keywords: ZnO, deep level transient spectroscopy, oxygen vacancy

(Some figures may appear in colour only in the online journal)

1. Introduction

ZnO is a very attractive semiconductor for optoelectronic uses. Its direct wide band gap (3.37 eV) and large binding exciton energy (60 meV) allow ZnO to compete with GaN for light emitting diode (LED) applications in the UV spectrum. To fabricate LED devices, the $n$- and $p$-doping processes must be fully mastered in order to control the conductivity and type of the active layers. Shallow donor levels responsible for the residual $n$-type conductivity of as-grown materials are commonly attributed to native point defects, hydrogen or period III elements (like Al, Ga or In). Formerly, the oxygen vacancy was believed to be one of these shallow states. However, recent theoretical works indicated that the oxygen vacancy ($V_O$) is not a shallow donor level but a deep donor level with a negative $U$ behavior and a $(2+0)$ charge transition in the energy range 1–2 eV below the conduction band edge $E_C$ [1–6]. Based on considerations about the $V_O$ formation energy, some authors found that the concentration of this defect should be low in as-grown $n$-type materials [1, 3], as confirmed by an electron paramagnetic resonance (EPR) experiment in which $V_O$ is detected only after irradiation treatment. The goal of this work is to detect the $V_O$ in $n$-type ZnO crystals grown by different techniques, one of which being implanted using the Fourier transform deep level transient spectroscopy (FT-DLTS) technique performed in a wide temperature range (80–550 K). Indeed, FT-DLTS is a well adapted technique because its sensitivity is at least one part per thousand of the background doping concentration, thus allowing the detection of trap concentrations as low as $10^{13}$ cm$^{-3}$.

This article is organized as follows: in the first part, the experimental details and FT-DLTS spectra of the five samples grown by different techniques are described. In the second part, the Arrhenius diagrams are analyzed. Finally, the properties of the deepest trap at $E_C - 1$ eV are discussed and an assignment to one of the electronic transitions taking place in the oxygen vacancy is shown to be plausible.

2. Experimental details

Five (0 0 0 I) oriented bulk ZnO samples were investigated in this work: sample #1 is grown by chemical assisted vapour phase transport (CVT) on a ZnO substrate, sample #2 is a CVT crystal grown on sapphire, samples #3 and #4 are hydrothermal (HT) ZnO crystals and sample #5 is a HT Nitrogen
Table 1. Description of the five samples investigated in the work (growth method, origin of the sample, additional remarks and effective doping $N_d – N_a$ evaluated from C(V) measurement).

| Sample | Growth method/Origin | Remark                | $N_d – N_a$ (cm$^{-3}$) |
|--------|---------------------|-----------------------|--------------------------|
| #1     | CVT on ZnO/Leti-CEA  | Homoeptaxial          | 3.0 × 10$^{15}$          |
| #2     | CVT on sapphire/Leti-CEA | Heteroepitaxial        | 1.6 × 10$^{16}$          |
| #3     | HT/Crystec Inc.     | No                    | 1.2 × 10$^{16}$          |
| #4     | HT/Tokyo Denpa Inc. | No                    | 3.0 × 10$^{16}$          |
| #5     | HT/Tokyo Denpa Inc. | Implanted             | 2.3 × 10$^{16}$          |

implanted one. Sample #1 is 700 µm thick while samples #3, #4 and #5 are 500 µm thick. Sample #2 is a slice around 700 µm cut out from a 7700 µm thick crystal grown on sapphire. Each face of this slice was then chemically and mechanically polished to remove the damaged subsurface and to ensure good surface quality. In case of sample #1, the polarity face was identified prior to the growth by using diluted HCl etching (O-face is much more sensitive than Zn-face) and/or by measuring the abrasion rate during the polishing process (two times higher in the case of O-face by comparison with Zn-face). In case of sample #2, a thin ZnO layer grown by organo-metallic vapor phase epitaxy onto a sapphire wafer composes the seed. The polarity of this template seed is Zn (confirmed through TEM and by chemical etching). In case of samples #3, #4 and #5, the substrate supplier indicated the face polarity, which has been checked by ourselves. The samples #1 and #2 were grown at 1030 °C [7] and then annealed at 1100 °C for one hour. The HT samples #3, #4 and #5 were annealed at 1100 °C. Then, the sample #5 was implanted with Nitrogen atoms (multi-implantation with energy ranging between 50 and 200 keV and a total dose of 2.2 × 10$^{15}$ cm$^{-2}$) and post-annealed at 900 °C. The characteristics of the five samples are summarized in table 1. All the samples were cleaned with organic solvents before being treated by remote oxygen plasma (ROP). Pt Schottky contacts (50 nm thick and 500 µm in diameter) were evaporated on the O-face of the five samples and full sheet Ti/Au ohmic contacts (20 nm/80 nm) were evaporated on the whole Zn-face in order to fabricate the ohmic contact of the diodes.

Capacitance voltage (C(V)) and deep level transient spectroscopy measurements were performed with Phystech FT1030 hardware and software. The internal bridge operates at a 1 MHz, a measurement frequency which has been checked to be lower than the cut-off frequency of all the diodes. FT-DLTS spectra were obtained from the fast FOURier transform (FFT) of the capacitive transients [8], delivering up to 28 Fourier coefficients for each time window. Current voltage (I(V)) measurements were firstly achieved to check the rectifying behavior of Pt contacts and the leakage current at different temperatures. C(V) measurements were then performed using reverse bias voltage to determine the effective doping level $N_d – N_a$. Finally, FT-DLTS analysis were performed between 80 and 550 K using reverse bias $U_r = −2$ V for samples #1 #2 #4 #5, $U_r = −4$ V for sample #3 and a pulse voltage ($U_p$) of 0 V for all the samples. For the five samples, different times windows ($T_w$) ranging between 1 ms and 1 s were used in order to collect numerous data, thus improving the accuracy of the Arrhenius diagram.

3. Results, analysis and discussion

3.1. Fourier transform deep level transient spectroscopy

A total of seventeen electron traps have been detected in the five samples. Typical FT-DLTS spectra are shown on figure 1. The Arrhenius diagrams shown in figure 2 were obtained by extracting both temperature and emission rates from the maxiima detected in DLTS spectra using up to 28 distinct and independent correlation functions yielding back as much Fourier coefficients. Letter labels have been assigned to the thirteen traps found in these five samples(from a to m). Four additional traps are indicated by a star on figure 1 and not reported on figure 2. These traps will not be discussed in this article. By linear fitting, the activation energy (from the slope) and the apparent capture cross section (from the ordinate at zero abscissa) have been determined using the standard emission rate formula:

\[
e_n = \frac{γ_n σ_n ν_n N_c}{kT} \exp \left( \frac{-E_a}{kT} \right)
\]

where $e_n$ is the emission rate, $γ_n$ the entropy factor assumed to be unity in this section, $σ_n$ the capture cross section, $ν_n$ the thermal velocity of electrons, $N_c$ the effective density of states in the conduction band, $E_a$ the activation energy, $k$ the Boltzmann constant and $T$ the temperature.

Data falling on the same lines in the Arrhenius diagram of figure 2 can be grouped into three ensembles of electron traps ((e, f), (g, h) and (i, j, k, l, m)) labelled [EX], where X is their activation energy in meV. The fact that the emission time constant of each ensemble is superimposed on the Arrhenius diagram strongly suggests that each of [E500], [E640] and [E1000] is related to a trap with the same physical origin and common to several samples.

The [E280] trap is only observed in sample #4 and commonly labelled E3 as reported in literature [9]. The electronic properties (activation energy ($E_a$) and apparent capture cross section ($σ_n$)) of the four electron traps [E280], [E500], [E640] and [E1000] are summarized in table 2. A unique fit has been done for each one using the data from the different samples.

It must be noticed that the numerous experimental data due to (i) the deep level transient fourier spectroscopy technique and to (ii) the number of samples, involve very weak error bars in the quantities extracted from the fit, irrespective of systematic errors discussed further. Three traps (a–c) with activation energies from 135 to 171 meV and rather low capture cross sections (from $5.3 \times 10^{-18}$ cm$^2$ to $4.0 \times 10^{-17}$ cm$^2$) have been observed in samples #1, #4 and #2. Some works [10–14] mentioned levels with such low energy but larger capture cross sections except in [15, 16]. The trap [E500] observed in samples #2 and #4 is often reported in the literature [17–21] and
commonly named E4 even if its attribution is still unclear. The trap [E640] has been observed only in samples #1 and #2, which are two CVT grown samples. This correlation with the preparation method probably means that this trap is linked to a specific impurity of the CVT process. In literature [15, 22], the rare possible occurrences of this trap are also reported in CVT samples.

The deepest [E1000] electron trap is systematically observed in the five samples. Since all the samples have been treated by a oxygen plasma, the possibility of introducing such a defect by this treatment has been considered. However, the depths investigated below the Schottky contact (see table 3) are too large to be affected by this treatment which is not at the origin of the traps observed in this work. The [E1000] activation energy and apparent capture cross section have been determined by doing a unique and simultaneous fit of experimental data from samples #1–3 and #5. The $E_{an}$ and $\sigma_n$ values deduced from the Arrhenius diagram have been then used to simulate the FT-DLTS spectra shown in figure 1(b), both obtained from the first real Fourier coefficient [8]. For the extraction of $E_{an}$ and $\sigma_n$ values of the [E1000] trap, data coming from the sample #4 were not taken into account. As
shown in figure 1, the peak of the [E1000] level of sample #4 is rather broad and probably contains the contribution of other levels, so that the relationship between the emission rate and the peak position of the FT-DLTS spectra becomes inaccurate.

For the four other samples, the good agreement between the experimental transient amplitude and the simulated one confirms the confidence given by the error bars and indicates that the [E1000] trap is a simple point defect in contrast to extended defects which generally result in more broadened spectra with respect to the Fourier transform of a purely exponential transient [23].

3.2. Electron emission from the oxygen vacancy V\textsubscript{O}

Among native point defects, the oxygen vacancy \( V_{O} \) is the only centre which shows thermodynamic transition levels calculated by \textit{ab initio} methods in the upper half of the band gap in most studies [1–4]. Another team of theorists [5, 6] found these transition levels in the lower half of the band gap, although all these authors agree both about the \( a_1 \) symmetry of the \( V_{O} \) states, mainly coming from the 4s dangling bonds of the four Zn neighbors which have essentially a conduction band character and the double donor nature of \( V_{O} \) with a negative correlation energy, making \( V_{O}^{2+} \) and \( V_{O}^{4+} \) the only stable states. The half of the two electrons transition energy \((E_{c} - E_{F}^{2+})\) (where the upper index holds for the numbers of trapped electrons before and after the transition) is close to 1.2 eV in the studies published by the former authors [1–4]. When the Fermi level is between the one electron transition energies \((E_{c} - E_{F}^{1+})\) and \((E_{c} - E_{F}^{2+})\) and the formation energy of \( V_{O}^{2+} \) is always higher than those of \( V_{O}^{0} \) and \( V_{O}^{4+} \), thus making \( V_{O}^{2+} \) unstable. In FT-DLTS, after the capture process resulting from the pulse voltage which makes the trap neutral, since the electron involved in the first ionization is bound more strongly than the second one, the second electron emission follows immediately the first one at a given temperature, resulting in a single peak in the DLTS signature with an amplitude multiplied by two [24]. Therefore, the single thermal activation energy \( E_{a n} \) measured in FT-DLTS, which is due to a single electron emission from \( V_{O}^{0} \) may be determined by \((E_{c} - E_{F}^{1+})\), which is larger than \((E_{c} - E_{F}^{0})\), the remaining electron being consequently emitted much faster. The situation was different for the initial and final charge states of defects with negative correlation energy previously known in other semiconductors, because they were either amphoteric in Si [24], double acceptors lying close to the conduction band in 4H-SiC [25] or double donors lying close to the valence band in Si [24]. Hence, a detailed analysis of the capture cross section derivation and theoretical calculations already published has to be addressed because it can be helpful to either validate or discard the assignment of the present [E1000] level to \( V_{O} \).

3.2.1. Electron emission related to the \( V_{O}^{0/1+} \) and \( V_{O}^{4+} \) transitions.

Taking both capture and emission kinetics and semiconductor statistics into account, the emission rates of the two transitions at thermodynamic equilibrium can be expressed respectively as

\[
e_{n2} = \gamma_{n2} \sigma_{n2} \exp \left( \frac{-\Delta H_{T}^{2+}}{kT} \right)
\]

Table 3. \[\text{[E1000]} \] trap density \( N_{t} \) deduced from the capacitance transient amplitude measured by deep level transient spectroscopy, combined to the \( N_{t} - N_{d} \) density from C(V), in the five ZnO samples and averaged on a depth ranging from the space charge region \( W_{p} \) (during pulse voltage \( U_{p} \)) to the space charge region \( W_{r} \) (after the pulse bias and under reverse bias \( U_{r} \)).

| Samples | \( N_{t} \) (cm\(^{-3} \)) | \( W_{p} \) (nm) | \( W_{r} \) (nm) |
|---------|-----------------|-------------|-------------|
| #1      | \( 2.6 \times 10^{14} \) | 750         | 900         |
| #2      | \( 4.2 \times 10^{14} \) | 300         | 470         |
| #3      | \( 6.4 \times 10^{14} \) | 440         | 460         |
| #4      | \( 1.2 \times 10^{14} \) | 450         | 500         |
| #5      | \( 3.6 \times 10^{15} \) | 330         | 450         |

Table 2. Activation energy \( E_{a n} \) and capture cross section \( \sigma_{t} \) of electron traps detected in the five different ZnO samples investigated in this work. The labels correspond to the ones of the Arrhenius diagram and DLTS spectra.

| Trap    | Label | \( E_{a n} \) (eV) | \( \sigma_{t} \) (cm\(^{2} \)) | Samples |
|---------|-------|--------------------|----------------------------|---------|
| [E280]  | d     | 0.278 ± 0.001     | 1.8 ± 0.2 × 10\(^{-16} \) | #4      |
| [E500]  | e, f  | 0.505 ± 0.006     | 2.5 ± 0.8 × 10\(^{-14} \) | #2, #4  |
| [E640]  | g, h  | 0.644 ± 0.005     | 4.6 ± 0.9 × 10\(^{-15} \) | #1, #2  |
| [E1000] | i, j, k, l, m | 1.018 ± 0.037 | 1.6 ± 0.4 × 10\(^{-13} \) | #3, #1, #2, #5, #4 |
for the $V_{O}^{0/1+}$ transition and

$$
\epsilon_{n}\frac{1}{2} = \gamma_{i} \sigma_{n0} N_{C} \exp \left( -\Delta H_{i}^{1/0} / kT \right) \tag{3}
$$

for the $V_{O}^{1+}/2^{+}$ transition, where $\sigma_{ni}$ is the capture cross section, $\gamma_{i}$ the entropy factor discussed in the following, $\Delta H_{i}^{1/1}$ the enthalpy of the transition, $i$ the number of trapped electrons, with $i = 0$ in the case of $V_{O}^{2+}$. The entropy factor $\gamma_{i}$ has two contributions: the degeneracy factor and the vibrational entropy. The neutral state $V_{O}^{0}$ is obtained if four electrons lie in the four $a_{1}$ states, with a total degeneracy of $m = 8$. Consequently, the configuration parts of the degeneracy factor, equal to the ratio of the number of possible combinations $C_{m}^{i+1} / C_{m}^{i+2} = \frac{m - i - 2}{i + 3}$ are respectively $5/4$ for $\sigma_{n0}$ and $2$ for $\sigma_{n0}$. The other part $\exp(\Delta S_{i,vibr}/k)$ of the entropy factor is due to vibrational entropy which reaches its maximum for band to band transitions and determines the temperature dependence $dE_{D}/dT$ of the band gap energy $E_{G}$ [26, 27]. From measurements of Rai and co-workers [28], $dE_{D}/dT$ is close to 0.1 meV K$^{-1}$ in the range 300–450 K, a value which induces upper limits of 1.25 for $\Delta S_{i,vibr}/k$ and 3.5 for $\exp(\Delta S_{i,vibr}/k)$. But the effective entropy change in the transition $\Delta S_{i,vibr}$ is much smaller because the levels are expected to follow the conduction band edge from which the states of $V_{O}$ originate and the transition energy is close to only one third of the band gap energy $E_{G}$. Therefore, the total entropy factors $\gamma_{0}$ and $\gamma_{1}$ would be very close to one, as previously assumed.

### 3.2.2. Capture cross section of the $V_{O}^{0/1+}$ and $V_{O}^{1+}/2^{+}$ transitions.

In equations (2) and (3), the capture cross sections $\sigma_{n0}$ and $\sigma_{n0}$ are dependent on the microscopic properties of the defect or impurity and temperature in the general case. Extensive theoretical calculations of the multi-phonons mediated transition probability per unit time and capture cross section of deep levels have been performed within the framework of the Born–Oppenheimer approximation from the seventies to the nineties [29–35]. These quantities are dependent on the average phonon energy $h\omega_{0}$ in a relative way because $h\omega_{0}$ has to be compared to the thermal energy $kT$, to the ionization enthalpy $\Delta H_{i}^{1/1} = p_{i} h\omega_{0}$ thus defining the number of phonons $p_{i}$ necessary for energy conservation and to the Condon shift $S h\omega_{0}$ where the Huang and Rhys factor $S_{i}$ scales the coupling between the phonon modes and the one electron states. The picture which emerged from these calculations allows to write the capture cross section as:

$$
\sigma_{ni} = \sigma_{n0} F \left( h\omega_{0} / kT, p_{i}, S_{i} \right) C_{2} \tag{4}
$$

where $\sigma_{n0}$ is the capture cross section limit for infinite temperature of a neutral center which directly depends on the matrix element of the non-adiabatic hamiltonian between initial and final states, $F \left( h\omega_{0}/kT, p_{i}, S_{i} \right)$ the line shape function of the optical spectrum for a zero photon energy and $C_{2}$ the averaged Sommerfeld factor, which takes into account the deformation of the wave functions induced by the Coulomb potential [29, 34]. From the analytic expression given in [32], the product $F \left( h\omega_{0}/kT, p_{i}, S_{i} \right)$ can be calculated and a thermal activation of the cross section can be inferred. For the oxygen vacancy in ZnO, the Huang and Rhys parameter can be assessed from the configuration diagram given in the figure 3 of [1]: close to $p_{0}/2$ in the transition $V_{O}^{0/1+}$ which involves the $\sigma_{n0}$ capture cross section measured in DLTS experiments and close to $p_{0}$ in the transition $V_{O}^{1+}/2^{+}$. Generally speaking, the prefactor $\sigma_{n0}$ is more difficult to assess because it is proportional to the matrix elements of the perturbative hamiltonian. It has been estimated in the range $10^{-13}–10^{-12}$ cm$^{2}$ by Henry and Lang [31] for most impurities and is taken to be $10^{-14}$ cm$^{2}$ by Pässler [29]. But as shown by Ridley [30], it is both proportional to $S_{2}^{2}$ and then increases with the electron–phonon coupling, which is rather high in $V_{O}$ since $S_{i}$ are of same magnitude as $p_{i}$ or $p_{0}/2$ and to the matrix element of the perturbative hamiltonian calculated by an integral over spatial coordinates of the wave functions of the bound electron and delocalized one. In the case of a vacancy, the wave function of the bound electron spreads over a much larger distance than for an impurity center because it is localized in the dangling bonds of the neighbouring atoms. This fact justifies that $\sigma_{n0}$ must amount to about $2 \times 10^{-13}$ cm$^{2}$ in order to fit the experimental value. The capture cross section $\sigma_{n0}$ involved in the transition $V_{O}^{0/1+}$ is expected to be even greater because the Huang and Rhys parameter $S_{0}$ and $Z=2$ are both higher than in the $V_{O}^{0/1}$ transition.

### 3.3. Discussion.

The emission rate inequality $\epsilon_{n2} \ll \epsilon_{n1}$ is confirmed both because $\epsilon_{n1} < \epsilon_{n0}$ and $\Delta H_{i}^{1/1} > \Delta H_{i}^{0/1}$, implying that only the slower ($\epsilon_{n2}$) emission events are detected in DLTS at all temperatures. This means that the electronic transition of the oxygen vacancy measured by DLTS is only characteristic to the $V_{O}^{0/1+}$ transition. Also, the capture cross section of the transition must correspond to a single positively charged center and the activation energy $E_{an}$ deduced from the Arrhenius diagram must be compared to the ($0+/1+$) transition calculated by \textit{ab initio} methods.

It must be noticed that the capture cross section which is deduced from an Arrhenius diagram is neither the effective one in the measurement temperature range nor the theoretical value $\sigma_{n0}$ at infinite temperature but an intermediate value obtained at the intercept of the tangent to the curve with the vertical axis located at infinite temperature. Consequently, in the case of $\sigma_{n0}$, the effective capture cross section in the temperature range of measurements is smaller but still in the range of the value given by the Arrhenius diagram due to the thermal activation of the $F \left( h\omega_{0}/kT, p_{i}, S_{i} \right)$ $C_{2}$ factor. Despite such a lowering, the real capture cross section cannot be measured directly because, taking into account the net doping concentrations given in table 1, the typical capture kinetic amounts to only some picoseconds (too short for measurement). Anyway, the order of magnitude of the capture cross section ($\geq 10^{-13}$ cm$^{2}$) of the trap measured in this work is in good agreement with a positively charged center (attractive for electron) like the $V_{O}$ which is the only native defect being related to an electronic state within the band gap with an attractive character for electrons in ZnO.

The measured activation energies are weaker than those calculated in previously quoted theoretical studies [1–4] by
some tenths of eV for the $V_{0}^{+}\varepsilon^{0}$ transition.\(^5\) But both because the systematic presence of the [E1000] trap implies an assignment to a native defect rather than an impurity and the oxygen vacancy is the only native defect which is an attractive centre for electrons, a 1 eV value assigned to the enthalpy of the $V_{0}^{+}\varepsilon^{0}$ transition of the oxygen vacancy is most probable. Moreover, the discrepancy between experimental and most of theoretical transition enthalpies [1–4] is noticeably smaller in comparison with Hofmann et al proposal \([36]\) which assigned the electron trap at $E_C - 530 \text{ meV}$ to the oxygen vacancy. It must be noticed that the assignment of the level at $E_C - 530 \text{ meV}$ to the oxygen vacancy is discarded by two important results reported in this work: (i) this level is found here (E500) in only two of the five samples studied in this work which is inconsistent with a native point defect like the oxygen vacancy, (ii) this level is found in sample #4 (not implanted) and not in sample #5 (same than #4 but implanted in the case of #5), in contradiction with the assignment to an oxygen vacancy created by implantation process.

The energy level reported by Quemener et al \([21]\) for the E5 trap is in good agreement with our results and seems to be also the $V_{0}$, except that the capture cross section is slightly lower. Unfortunately, the Arrhenius diagram has not been shown, preventing the detailed comparison with the five Arrhenius diagrams reported in the present work. Future works will be needed to confirm the assignment of the $V_{0}^{+}\varepsilon^{0}$ to the [E1000] trap. Indeed, the possibility that the [E1000] trap is related to a complex between an impurity (present in ZnO whatever the growth method, most probably H) and a native defect (created by implantation for the particular case of this work consisted to show that only the deepest level is found here (E1000)) with Hofmann et al \([21]\) for the $E_{5}$ \(1/2\). But both because the discrepancy between experimental and most of theoretical transition enthalpies [1–4] is noticeably smaller in comparison with the assignment to an oxygen vacancy created by implantation process.

4. Conclusions

Traps have been detected and their parameters extracted from FT-DLTS data in five different n-ZnO samples. A salient feature of this work consisted to show that only the deepest level is found here (E1000), with a ionization energy of 1 eV for electrons and a very probable donor character due to its very large capture cross section, turns out to be present in all the five samples, in contrast to other deep levels. From a detailed analysis of the electronic properties of the multi-phonons mediated transitions taking place in the oxygen vacancy and comparison with our experimental results, we can conclude that the capture cross section and ionization energy deduced from the experimental Arrhenius diagram are compatible with those estimated from theoretical considerations pertaining to the oxygen vacancy in ZnO, which is recognized as a double donor with a negative correlation energy.

\(^5\) The numerical simulations showed that the thermal activation of the cross section, included in the $F(h\nu/kT, p, S) C_p$ factor, can be neglected in comparison with the activation energy $E_a$ measured in this work considering phonon energy at 40 meV.

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