Indian Journal of Pure & Applied Physics
Vol. 60, May 2022, pp. 401-406

Femto Seconds Laser Based Efficient THz Generation from Different Temperature Annealed CdTe Thin Films and Effects of Carrier Concentration and Phase Transition on Efficiency of Generation

M Mahendar, R N Vamsi Krishna & A K Chaudhary*

Advanced Center for Research in High Energy Materials, University of Hyderabad, Hyderabad-500 046, India

Received 16 February 2022; accepted 19 April 2022

The paper reports the thermal evaporation based growth process of CdTe thin films on glass substrates. These films were annealed between room temperature to 200, 300 and 400 °C, respectively. The XRD characterization of these films revealed the change in crystalline phase from cubic to triclinic above 200 °C. Finally, these films were subjected to 800 nm wavelength of 35fs pulsed obtained from Ti: sapphire amplifier at 1kHz repetition rate. The incident power of the laser was focused and tuned between 150-350 mW range and generated THz signals were recorded using calibrated Pyroelectric detector at 22.5 Hz frequency. The highest power of the THz signal was 80nW for 200 °C annealed film with respect to incident power of 300mW. The highest efficiency of THz signal was of the order of 3.11E-5%. We have also explained the effect of carrier concentration and phase transition with respect to different annealed temperature for efficient generation of THz signal.

Keywords: Cadmium Telluride; Thin films; Tera-Hertz Generation; Carrier concentration; X ray Analysis; Phase transition

1 Introduction

Cadmium telluride (CdTe) is one of the most prominent polycrystalline materials for thin film solar cell because of its physical properties. It can be prepared with a high conductivity in both n and p type forms. CdTe is a member of the II–VI family of compound II-VI periodic group optically active chalcogenide semiconductor materials with immense applications in optoelectronics, photonics and bio-labelling applications.Intervention of nanoscience and nanotechnology has enabled the realization of low dimensional nanostructures of Cadmium chalcogenide (CdS, CdSe, or CdTe) with the enhanced surface area to volume ratio that has attracted major appreciation with their unique and enhanced electronic and optical properties[1-5].Being a direct bandgap semiconductor with the high atomic number and electron density, CdTe has been widely used in photovoltaic, sensors, diodes, rectifiers, and detectors[6–9] One of the interesting properties of CdTe is its high bond energy (5.75 eV)[10] which makes it a perfect candidate for space applications too. Looking at the material consumption point of view, the efforts are being made in the direction of the fabrication of ultra-thin film and small area devices[11]. Recently, Chu *et al.* have demonstrated that the solar cell efficiency of 8% from only 250 nm CdTe absorber layer[12]. The fabrication process also plays an important role in the final costing of the device. Though the conventional vacuum techniques lead to a better quality device, the low-cost alternatives are the area of interest to the researchers. CdTe has the possibility to be doped both n- and p-type and the variety of preparation techniques such as thermal evaporation which often preferred because it offers large possibilities to modify the deposition condition. The techniques like electrodeposition, spin coating, chemical bath deposition are being commonly used now a day for the synthesis of high-quality nanoparticles, thin films, or even large area devices.

Sergi *et al.* reported the effect of annealed temperature on the optical properties of P doped CdTe films [13-14]. Kasmorski *et al.* have reported the use of Auger analysis of CdSCuInSe2 thin-film used for the solar cells applications[15]. Pankove has nicely discussed the utility of five important properties in the deposition of CdS semiconductor films These studies were conducted by means of optical characterization, pH measurements, energy consumption tests, and chemical analysis[16]. Hans Batch and Dieter Krause have well discussed the art of deposition of semiconductor films on glass and their optical characterizations[17]. Sivaramakrishna *et al.* have explained the phenomena

*Corresponding author:
(E-mail: akcphys@gmail.com, akcsp@uohyd.ernet.in)

of instability in resistance and variation of the activation energy with thickness and deposition temperature in the case of $CdSe_{0.6}Te_{0.4}$ film[18].

The development of thin films has helped in solving many problems in non-linear optics. In the non-linear processes phase matching condition is one of the definitive criteria to achieve results. The coherent length plays a crucial role in this aspect. The growth of Nano-structure in making of thin films reduced the barrier of coherent length. This provided a new gate in developing efficient THz sources.

Efficient THz sources can be developed using thin films which are operated using optical rectification and photo-dember effect. Band-gap and the thickness of the material used in thin films plays a crucial role in production of commercial THz sources. Some interesting semiconductor or organic crystals such as ZnTe, $ZnGeP_2$, GaAs, GaP, BNA, DAST *etc*. are widely used for the THz generation. The CdTe in form of a single crystal or thin film that can be used for the generation of efficient THz signal in very effective manner[19-23]. However, in previous report the authors have presented the qualitative picture of THz generation from CdTe films. The report could not able to establish the role of carrier concentration with respect to annealed temperature and corresponding phase changes occurred in context of THz generation. In addition, the information of the efficiency was also not ascertained. The temperature at which the thin films were annealed also provides valuable information related to structural changes that is directly correlated to the efficiency of the generated THz signal.

However, second harmonics and THz generation from centrosymmetric materials are related to induced electric field based broken symmetry. Which is basically a surface phenomenon[24-26]. The entire process of generation from Centrosymmetry thin films is governed by second order nonlinearity and surface current induced due to third order nonlinearity and also known as Photo- dember effect. Equation (2 & 3) clearly represent the process of generation from the thin films.

$$P_i(\Omega) = \chi^{(2)}_{eff,ijk}(\Omega; \omega + \Omega, -\omega)E_j(\omega + \Omega)E^*_k(\omega) \quad \ldots (1)$$

$$\chi^{(2)}_{eff,ijk} = \chi^{(2)}_{ijk} + \chi^{(3)}_{ijk}E_{surf,l} \quad \ldots (2)$$

The generation of polarized waves in THz domain due to combined effect of Optical rectification process and effect of broken symmetry are explained using Eq.1 in which E and ω are electric field and frequency of excitation pulse, Ω is the frequency of the generated pulse and i, j, k are polarization directions. For efficient THz generation we should achieve a resonance condition between ω and Ω. In the current experiment we have used the excitation pumping source femto-seconds pulses which is responsible for the generation of ultra-short time based charge carriers that matches to time scale of THz signal.

In photo-dember process, χ^3 plays a very crucial role in generation of THz pulses which is shown in Eq.2. The value of the χ^3 depends on the symmetric nature of the crystalline thin film. The Centro-symmetry of the cubic structure increases the involvement of the process in generating efficient THz pulses. The decrease in symmetry of the crystalline structure reduces the value of χ^3 and affecting the strength of THz signal.

In the past, several groups have reported generation of THz signal using CdTe crystals and thin films and studied the effects of temperature in various parameters of CdTe crystal. This helped us to prove that at higher temperatures the refractive index, transmittance and formation of different states are varying with temperature. This also proved that CdTe can also be used as commercial efficient THz source.

In the present report, we have discussed the detailed characterization and optical behavior of CdTe thin films annealed at different temperatures. Further, we have observed the intensity and efficiency of output THz signal by CdTe thin film for different input powers at 800nm. We also observed the variation of physical structure and its effects on efficiency of the thin film when annealed at 4 different temperatures *i.e*. 27 , 200 , 300 and 400 ^{o}C, respectively.

2 Experimental Procedure

The experiment was carried out in three parts. In the first part, the CdTe films were deposited and annealed at different temperatures. The second part deals with the XRD characterization for structural analysis while, the third part covers the experimental details of THz generation and recording of generated signals with respect to incident laser power.

(I) Growth procedure of annealed CdTe thin films

The samples were prepared by a thermal evaporation method using a vacuum evaporation

(HINDHIVAC Vacuum coating unit, Model No: 12A4U), in high vacuum (10^{-6} Torr). The solid form of Cadmium (Cd) and Tellurium (Te) was used as source material and Glass slides were used as substrates to prepare cadmium telluride (CdTe) thin films of thickness around 50 nm. These films are deposited at a rate of 0.1 nm/sec on well-cleaned glass substrates. The substrates are pre-cleaned using chromic acid, acetone and distilled water through the systematic mechanism. The thickness and the rate of deposition of thin films were recorded using microprocessor-the controlled quartz crystal thickness monitor during deposition of films. The error in thicknessof the film is 0.2 nm.

(ii) XRD characterization of CdTe films

The XRD analysis was done for CdTe thin films annealed at different temperature using XRD X'pert PRO, PANalytical for its structural, morphological. In this the visible peaks were matched to known peaks of crystal structures. We determined the directional cosines of the crystalline structure in the thin film.

(iii) THz generation Setup and analysis

The Out-put THz radiation is observed by using a home-built THz radiation generation setup which is shown in the Fig.1 below.

THz radiation of CdTe films were measured using 800 nm wavelength pulses of 35 fs duartion at 1 kHz repition rate obtained from Ti:Sapphire laser amplifier. The incidient laser power was attenuated with λ/2 waveplate attenuator. The beam was focussed by 25 cm focal length lens and film was placed at loosly focus point. The film was rotated vertically using rotator to align it for the maximum generation of THz radiation. The genarted THz radiation is the mixture of unconveretd 800 nm wavelength which was separated using Teflon filter and silicon palte . The generated THz power is measured using pyrodetector (gentec Made) at room tempertaure. The output of the detector was fed to the lock-in amplifier and strength of the genearted power is mesured using computer. For increasing the signal to noise ratio (S/N) the laser pulses were chopped with 22 Hz range.

The incident laser power at 800nm was varied from 150 to 300 mW range with an increment of 25mW. The experiment is repeated for thin films annealed at different temperature.

The output radiation is characterized as a function temperature and incident input power. The carrier concentration is calculated from the standardized material parameters as a function of temperature. The efficiency and intensity were plotted with respect to incident power at different annealed temperature.

3. Results and Discussion

3.1 Result

The X-ray diffraction (XRD) results of the CdTe thin film deposited on the glass substrate at different annealing temperature are shown in Fig. 2. A crystalline cubic structure (confirmed with JCPDS #071-4163 and # 071-4162) and Anorthic (triclinic) structure were also revealed (confirmed with JCPDS

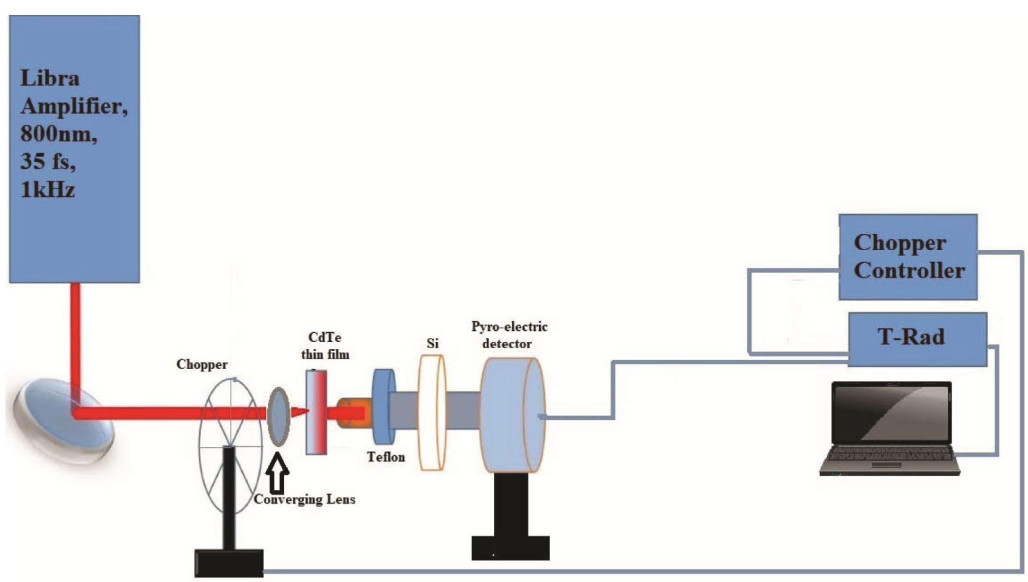

Fig. 1 — Schematic diagram Layout for THz generation and detection.

#055-0529). The 2θ values of 22.48°, 45.85° and 71.43° were matched with the cubic structure corresponding to (1 1 1), (3 1 1) and (4 2 2) index planes respectively. Peaks pointing at 22.43°, 32.88°, 45.85°, 55.65° and 71.41° correspond to the cubic structured index plane at (2 0 0), (2 2 0), (2 2 2) and (4 2 0) respectively. In addition, the peaks at 22.43° corresponds to dual crystalline phases *i.e.*, (111)/ (311) and (200)/220) index planes for cubic structures respectively. Fig. 2(d) shows the XRD graph of structured CdTe. The peaks at 27.94°, 32.90°, and 46.18° corresponds to the (2 0 1), (0 3 0), (1 4 2) planes for the crystal Anorthic (triclinic) structure. Overall, XRD graphs in Fig. 2(a) & (b) indicates that cubic phase. However, there were no peaks associated with the other compound of Cd or Te. In addition, the films exhibited a strong (1 1 1) plane peak, regardless of the thermal vacuum technique, which suggested that the CdTe crystallites had a cubic structure highly oriented with the (1 1 1) direction perpendicular to the glass substrate surface. Fig 1(a) & (b) show almost same peaks occurs but 300 °C show a mixed orientation (1 1 1) and (2 0 0) occurred. As the increase annealing temperature from 300 to 400 °C range, the intensity of the (1 1 1) peak get disappeared whereas at 300 °C two numbers of peaks appeared which clearly suggest the phase transition from cubic to anorthic (triclinic) structure. This indicates improvement of the crystallinity and/or increment of the degree of preferred orientation. Meanwhile, further increase of the Annealing temperature at 400°C resulted in smaller XRD peaks, indicating deterioration of the crystallinity.[23]

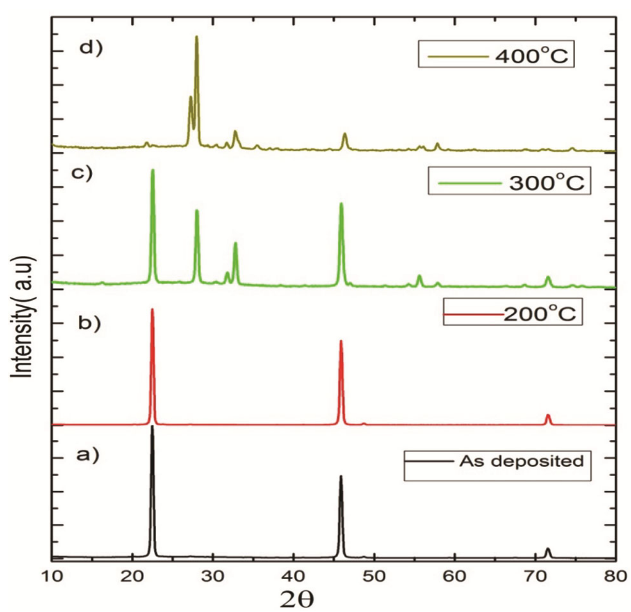

Fig. 2 — XRD pattern of the deposited CdTe thin film a) As-deposited b) 200 °C c) 300 °C d) 400 °C.

The carrier concentration was increased from $8*10^5$ to $8.013*10^{12}$ when annealed temperature is increased from 300K to 673 K. This indicates that carrier lifetime is getting decreased and more possibility of intra-band transitions.

The carrier concentrations are calculated using the standard equation. Which is given below:

$$n_i^2 = N_c N_v e^{\frac{-E_g}{k_B T}} \quad \ldots (3)$$

The intensity of the output THz radiation is increased with the increase in incident power. The drastic increase in the output power when the thin film is annealed at 200 °C is mainly due to increase in carrier concentration without any distortions in the film. The decrease in intensity after 200 °C is due to phase transitions from cubic to triclinic.

3.2 Discussion

Figure 2 shows that XRD spectra of CdTe films grown at different annealed temperature. This confirms the cubic structure in (1,1,1) between room temperature to 200 °C. But the phase started to transit from cubic (1,1,1) to triclinic phase (2,0,0) above 200 °C. This led to decrease the intensity of the THz generation for temperatures above than 200 °C.

Fig. 3 shows the increase in carrier concentration with respect to temperature. The curve shows exponential growth. This can be explained using Eq.No.3. The graph also shows a saturation behaviour at 400 °C temperature.

In addition, the observed optical energy band gap is located at approximately 1.5eV [26] which indicates the

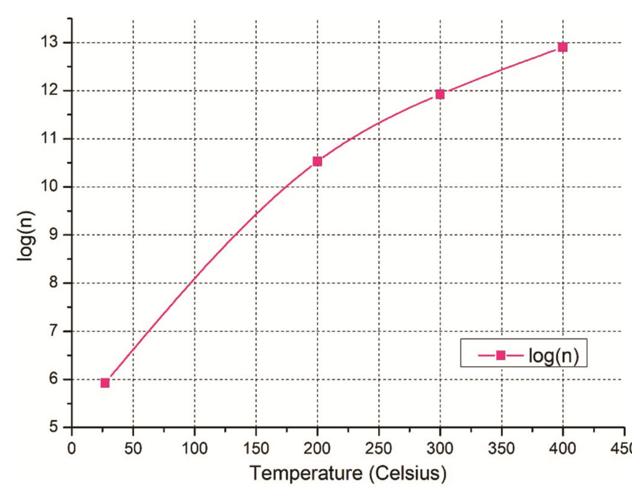

Fig. 3 — Shows the log (carrier concentration) *vs* temperature.

shift of Fermi energy level and also influenced the process of THz generation due to ultrafast transition. The increase in carrier concentration with respect to the temperature of annealed CdTe films resulted in enhancement of THz intensity. Fig.4 shows the intensity of generated THz radiation with respect to the incident power of femtoseconds pump laser beam. The intensity of generated signal was increased from 254.8nW/cm^2 to 1082.8nW/cm^2 at 200 ^{o}C annealed sample which is almost 3.7 times higher than the room temperature grown CdTe.

It is also shown in Fig. 5 that the efficiency of the generated THz signal is decreasing with respect to increase in the incident laser power below the temperature of 200 ^{o}C and showing a Gaussian behaviour above 200 ^{o}C. The decrease in efficiency is mainly caused due to formation of plasmons. The formation of plasmonic states is responsible for change in refractive index of the medium which also reduces the transmittance of the thin film. The phase transition above 200 ^{o}C also attributed to anomaly behaviour of efficiency of the thin film. It is also due to change of transmission behaviour *i.e*. drop in the transmission to change in the temperature due to high laser power density.

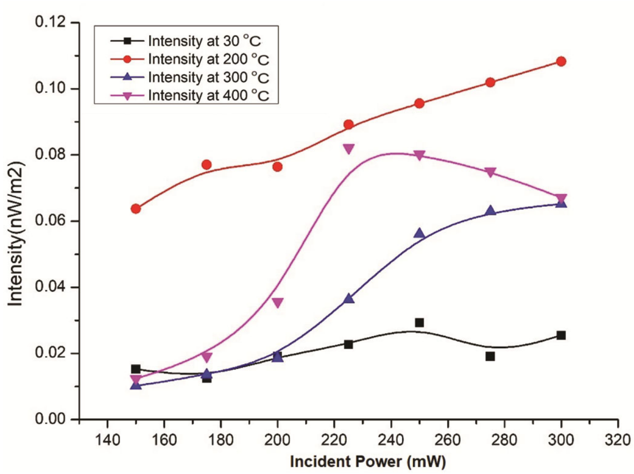

Fig. 4 — Depicts the variation of Intensity of THz radiation with incident power at different annealed temperatures.

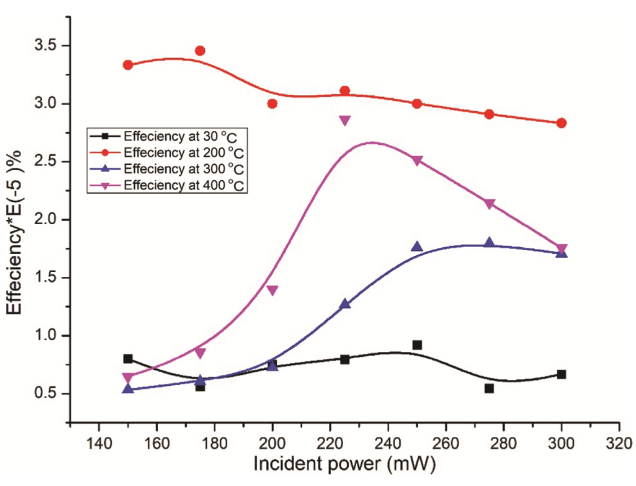

Fig. 5 — Shows the variation of Efficiency of the generated THz radiation with respect to the incident laser power at different annealed temperatures.

We have shown the role of symmetry in generating THz involving photo-dember effect in the CdTe thin-films annealed at different temperatures. The phase change after 200 ^{o}C from cubical to triclinic is losing the Centro-symmetry making the contribution of χ^3 less. This in turn reduces the power of recorded THz signal.

4 Conclusions

We have successfully deposited CdTe films using CVD technique and annealed them at different temperatures up to 400 ^{o}C. The XRD analysis proves that there is a change in phase of the thin film beyond 200 ^{o}C from cubic [mostly (1,1,1)] to triclinic [mostly (2,0,0)]. The intensity of the THz radiation is increased by 1.7 times with increase in incident power at as deposited temperature and at 200 ^{o}C The intensity of THz signal is showing Gaussian like behaviour for temperature above 200 ^{o}C, with increase in incident power. The change is crystal structure after 200 ^{o}C reduced the intensity of THz radiation compared to the lesser temperatures. The efficiency of the CdTe thin film is increased by 4.31 times when annealed at 200 ^{o}C than at room temperature. Above the temperature 200 ^{o}C efficiency is decreased. At all temperatures the efficiency of generation of THz radiation is decreased with increase in incident power. This may be attributed to formation irradiative phonon and plasmonic states in the film due to highly focused laser beam.

Acknowledgements

The authors would like to express their thanks to the funding agency Defence Research and Development Organization (DRDO), Ministry of Defence, Govt. of India for financial support under the grant No. DRDO/18/1801/2016/01038: ACRHEM-Phase-III and Dr. D. Ganesh for assistance during the experiment of THz generation.

Conflicts of Interest

Declare conflicts of interest or state "The authors declare no conflict of interest."

References

1 Z Tang, N A Kotov & M Giersig, *Science*, 297 (2002) 237.
2 Ma C & Wang Z L, *Adv Mater*, 17 (2005) 323.
3 Kar S, Satpati B, Satyam P V & Chaudhuri S, *J Phys Chem B*, 109 (2005) 19134.
4 Zhao T, Fang X, Li L, Bando Y & Golberg D, *Nanoscale*, 2 (2010) 168.
5 Duan X, Huang Y, Agarwal R, Lieber C M C M & Fast C G, *Nature*, 421 (2003) 241.
6 Cola A & Farella I, *Appl Phys Lett*, 102 (2013), 113502.
7 Singh V P, Ericson O M & Chao J H, *J Appl Phys*, 78 (1995) 4538.
8 Chen M C & Bevan M J, *J Appl Phys*, 78 (1995) 4787.
9 Solanki C S, Solar Photovoltaics, Fundamentals and Applications (PHI Learning, 2009).
10 Sinha S, Chatterjee S K, Ghosh J & Meikap A K, *J Appl Phys*, 113 (2013) 123704.
11 Paudel N R, Wieland K A & Compaan A D, *Sol Energy Mater Sol Cells*, 105 (2012) 109.
12 Chu T L, Chu S S, Pauleau Y, Murthy K, Stokes E D & Russell P E, *J Appl Phys*, 54 (1983) 398.
13 Segui Y, Carrere F & Bui A, *Thin Solid Films*, 92 (1982) 303.
14 Moss T S, Optical properties of semiconductors, Butterworths, London, (1957).
15 Kasmorski L L, Cooper R B, White F R & Merrill A J, *IEEE Trans Electron Devices*, 24 (1977) 496.
16 Pankove J I, Optical processes in semiconductors (Dover Publisher Inc, New York, (1971).
17 Bach H & Krause D, Thin Films on Glass, Springer – Verlag Berlin, Heidelberg, (1997).
18 Sbastian P J & Sivaramakrishnan V, J Appl Phys, 65 (1989) 237.
19 Zhang X C, Jingzhou X, Introduction of THz wave photonics, (Spienger).
20 Dalapati P, Manik N B & Basu A N, *J Semiconduct*, 34 (2013).
21 Sze S M & Kwok K N, Physics of Semi-conductor devices, 3rd Edn, by Wiley (2003).
22 Kumari Archana, Chaudhary A K & Venkatesh M, *Appl Opt*, 59 (2020) 3417.
23 Mahendar M, Chaudhary A K, Damrala G & Gupta V, Workshop in Recent Advances in Photonics 2019 (2019) 1.
24 Shen Y R, The principle of Nonlinear Optics, Wiley-Interscience: New York, 1984.
25 Zhu L G, Kubera B & Mak F K, *Sci Rep*, 5 (2015) 10308.
26 Strauss A J, *Rev Phys Appl*, 12 (1977) 167.