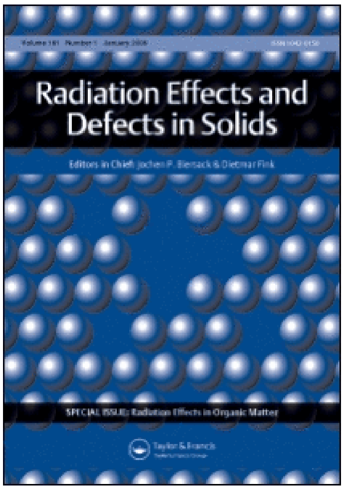
This article was downloaded by: *[INFLIBNET India Order]*
On: *7 October 2009*
Access details: *Access Details: [subscription number 909277354]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Radiation Effects and Defects in Solids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713648881

# DEGRADATION IN POLYTETRAFLUORO ETHYLENE BY 62MeV PROTONS

S. P. Tripathy [a]; R. Mishra [a]; K. K. Dwivedi [b]; D. T. Khathing [a]; S. Ghosh [c]; D. Fink [c]
[a] Department of Physics, North-Eastern Hill University, Shillong-793 022, India. [b] Arunachal University, Rono Hills, Itanagar-791 111, India. [c] Hahn-Meitner Institute, Glienicker Strasse 100, D-14109 Berlin, Germany.

Online Publication Date: 01 January 2002

**To cite this Article** Tripathy, S. P., Mishra, R., Dwivedi, K. K., Khathing, D. T., Ghosh, S. and Fink, D.(2002)'DEGRADATION IN POLYTETRAFLUORO ETHYLENE BY 62MeV PROTONS',Radiation Effects and Defects in Solids,157:3,303 — 310

**To link to this Article: DOI:** 10.1080/10420150212993

**URL:** http://dx.doi.org/10.1080/10420150212993

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Radiation Effects and Defects in Solids*, 2002, Vol. 157, pp. 303–310

# DEGRADATION IN POLYTETRAFLUORO ETHYLENE BY 62 MeV PROTONS

S. P. TRIPATHY[a,]*, R. MISHRA[a], K. K. DWIVEDI[b,c,†], D. T. KHATHING[a],
S. GHOSH[c] and D. FINK[c,]

[a]*Department of Physics, North-Eastern Hill University, Shillong-793 022, India;* [b]*Arunachal University, Rono Hills, Itanagar-791 111, India;* [c]*Hahn-Meitner Institute, Glienicker Strasse 100, D-14109 Berlin, Germany*

*(Received 4 January 2002; In final form 25 January 2002)*

The aim of our study is to describe the dose dependent proton induced modifications in Polytetrafluoro ethylene (PTFE) by using Fourier Transform Infra-red spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and X-ray diffraction analysis (XRD). The shifting of the main peak along with a decrease in its intensity, the decrease in thermal stability and melting point and the formation of stable free radicals were observed in the polymer by proton irradiation.

*Keywords*: Polytetrafluoro ethylene; Proton irradiation; Thermal stability; Degradation

## 1 INTRODUCTION

The mechanism of the interaction between protons and macromolecules is rather complicated. Many processes, such as the production of primary and secondary radicals, lead to the formation of double bonds and transformation of C—C bonds, and autoxidation occurs in the presence of oxygen. These reactions depend on the proton dose as well as on the environmental conditions during and after irradiation [1]. Both cross-linking and degradation take place during proton irradiation and are closely related to the irradiation dose. At certain doses, cross-linking becomes predominant and mechanical properties are improved. Irradiation of 62 MeV protons on Polypropylene and Polytetrafluoro ethylene showed a decrease in their optical band-gap, whereas no effect on the optical properties was observed in Polyethylene terephthalate and Polyimide [2]. 62 MeV proton irradiation was also found to modify the track registration properties of Polyallyl diglycol carbonate (PADC) by fullerene destruction [3] as well as by the use of thin metal foils in contact with its surface [4]. The study of solubility changes for poly(methyl methacrylate) as a function of fluence of 1.5 MeV protons has been reported [5]. 100 keV proton irradiation of polypropylene leads

---

* E-mail: samtripathy@anpa.it
[†] Corresponding author. Fax: +91 360 277317; E-mail: kkdau@hotmail.com
E-mail: fink@hmi.de

ISSN 1042-0150 print; ISSN 1029-4953 online
DOI: 10.1080/10420150210000005171

to cross-linking between the macromolecules of the polymer enhancing its mechanical properties [1]. The dose dependent modification of PADC by 62 MeV proton irradiation has been studied and it was found that the crystallinity and the thermal stability of the polymer decreased as a function of dose, whereas there was no change in the optical band-gap of the polymer [6].

Polytetrafluoro ethylene (PTFE) is a vinyl polymer, and its structure, if not its behaviour, is similar to polyethylene. It is made from the monomer tetrafluoroethylene by free radical vinyl polymerization. PTFE shows a remarkable chemical resistance and it is insoluble in all known solvents. It is attacked only by molten alkali metals and by fluorine at high temperatures. PTFE is incombustible and may be used up to 260 °C (300 °C for short periods). Its coefficient of friction is extremely low. Torissi and Foti (1996) [7] exposed the PTFE foils to MeV helium and proton beams and found that the irradiation of fluoro polymers produced a strong sample erosion with emission of fragments produced along the ion track. In the present work, a systematic investigation is done to analyse the effect of proton irradiation on PTFE as a function of dose.

## 2 EXPERIMENTAL DETAILS

### 2.1 Target Preparation and Proton Irradiation

Forty pieces of PTFE (composition: $C_2F_4$, density: 2.2 g cm$^{-3}$) of sizes (1 × 1) cm$^2$ were cut from commercially available sheets. The thickness of the polymer was measured by sensitive Heidenhain device and was found to be 200 ± 0.1 μm. The samples were washed thoroughly with soap solution and deionised water. The cleaned samples were then dried inside a vacuum desiccator. Four stacks were prepared containing 10 pieces of PTFE in each stack. Each stack was covered at both the ends by radiation sensitive Polyvinyl acetate (PVA) to check the uniformity of the impinging beam by its colour change. These were separately irradiated in presence of air to four different doses, *viz.* 10 kGy, 30 kGy, 60 kGy and 80 kGy by a 62 MeV proton beam from the heavy ion accelerator of the Ion Beam Laboratory "ISL" of the Hahn Meitner Institute (HMI), Berlin. The collimated proton beam of dimension (0.3 × 1) cm$^2$ passed perpendicularly through each stack.

### 2.2 Polymer Characterisation

The pristine and the irradiated samples were characterised by the following techniques.

### *2.2.1 X-ray Diffraction Analysis (XRD)*

X-ray diffraction patterns were recorded using the Cu-K$\alpha$ ($\lambda = 1.54$ Å) radiation with 8.04 keV energy from the Rigaku $\theta$–$2\theta$ X-ray spectrometer at Inter University Consortium, Indore, India. A rotating anode source and a Sodium Iodine scintillation detector have been used. The value of the diffraction angle ($2\theta$) ranged from 3° to 90° with a step size 0.04 mm. The measurements were done at room temperature and ambient pressure conditions. Each experiment was repeated at least twice and with both faces of the specimens alternatively exposed to the incident X-rays to check the reproducibility.

### 2.2.2 *Fourier Transform Infra-red Spectroscopy (FT-IR)*

The FT-IR spectra of all the samples were recorded in transmission mode using a Fourier transforming instrument (model NICOLET, IMPACT 410) keeping air as reference. All the measurements were done in the wave number range of 4000 to 500 $\mathrm{cm}^{-1}$ to study the structural changes including the alteration in position and intensity of the characteristic bands with an accuracy better than ±1% to ±3%.

### 2.2.3 *Electron Spin Resonance Spectroscopy (ESR)*

The ESR measurements were performed with a Varion (E-109, X-band) spectrometer with 100 kHz field modulation. The samples were placed in a quartz tube and the spectra were recorded at room temperature. The spectrometer worked at 9.6 GHz frequency with the following set up: Field Set: 3382 Gauss, Scan range: 1000 Gauss, Time constant: 0.25 sec, Scan time: 4 minutes, Modulation amplitude: $0.5 \times 1$, Receiver Gain: $6.3 \times 10^4$, Microwave power: 2 mW.

### 2.2.4 *Thermal Analysis*

A Perkin Elmer Delta series Thermal Analysis system was used to conduct Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The samples were cut into very small pieces, crimped in small aluminium pans and weighed in a microbalance. The samples were then heated at a predetermined rate of 20 °C/min with $N_2$ as the flushing gas.

(i) *Thermogravimetric Analysis* (*TGA*)
The samples were heated from 30 °C to 600 °C, and the thermograms, *i.e.*, the plot of weight percentage (ordinate) as a function of temperature (abscissa) were recorded within an accuracy of ±2 °C.

(ii) *Differential Scanning Calorimetry (DSC)*
The hermetically sealed samples were heated from 50 °C to 500 °C and the thermograms, *i.e.*, the plot of heat flow (Y-axis) versus temperature (X-axis) were obtained within the instrumental error of ±2 °C.

## 3 RESULTS AND DISCUSSION

The results obtained from the above mentioned experiments are described below.

### 3.1 X-ray Diffraction Analysis

The structures of pristine PTFE and the samples irradiated at the highest dose (80 kGy) were analysed by X-ray diffraction studies. The XRD spectra are shown in Figure 1 and the various parameters assigned with the peaks are given in Table I. The result showed that intensity of the main peak (A) (at $2\theta = 21.79°$ for the pristine material) was reduced and shifted up to $2\theta = 17.90°$ for the PTFE samples irradiated to the highest proton dose (80 kGy). The intensity of the other two peaks (B and C) also decreased after irradiation. That decrease denotes some destruction of the orderliness of the original crystal structure due to proton irradiation. Some new peaks (D and E) also emerged at $2\theta = 72.57°$ and 75.54° after irradiation (80 kGy), suggesting a partly buildup of new crystalline matter–though of very low intensity. Such an effect had been observed also at other occasions [8].

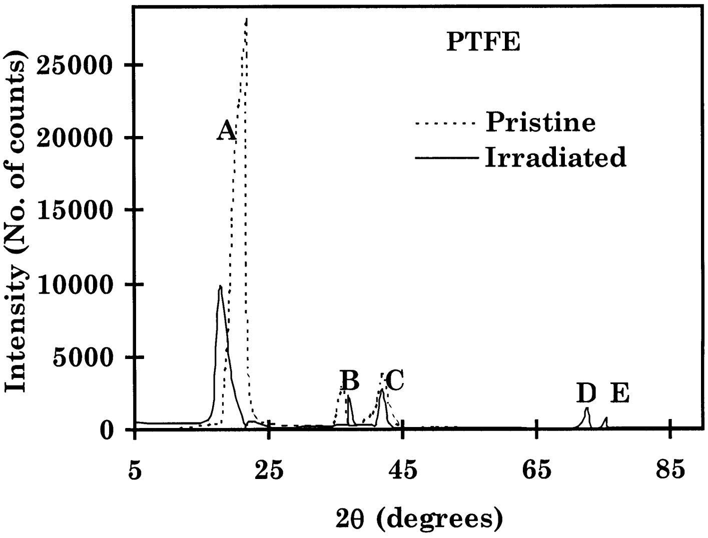


FIGURE 1 XRD spectra of the pristine and the proton irradiated PTFE (80 kGy).

## Fourier Transform Infra-red Spectroscopy

The FT-IR spectra of the pristine and the proton irradiated (80 kGy) PTFE are shown in Figure 2. The absorbance peaks from 1000 $cm^{-1}$ to 1300 $cm^{-1}$ (C) are contributions of the C-F stretching vibration [9]. Some new peaks emerged in case of the irradiated PTFE samples. The new peak at 1885 $cm^{-1}$ (A) originates from the carbonyl fluoride group (—COF) and that at 1795 $cm^{-1}$ (B) is assigned to $CF_2=CF_2$ terminal double bond vibration [10, 11]. Here, the structure of the polymer might be visualised as polyethylene with all its hydrogen atoms substituted by fluorine, where the C—F coupling was less covalent than the C—C coupling due to more electronegativity of fluorine. This made the C—C bond relatively less probable towards cleavage.

## 3.2 Electron Spin Resonance Spectroscopy

The ESR spectrophotometer recorded a signal of free radical formation for the polymer irradiated to the highest dose. The spectra are shown in Figure 3. The width of the signal formed was around 50 Gauss, which is usually attributed to $\sigma$-bonds. Since the irradiation was done in the presence of oxygen, a number of radiolysis products were formed. Especially $CF_4$ and $C_2F_6$ become less abundant in favor of $COF_2$. As reported by Spinks and Woods

TABLE I Position ($2\theta$), Intensity (I) and Full Width Half Maximum (FWHM) of the XRD Peaks of the Pristine (P) and the Proton Irradiated PTFE (80 kGy).

| | *2θ (degree)* | | *$I_{rel}$* | | *I (CPS)* | | *FWHM (degree)* | |
|---|---|---|---|---|---|---|---|---|
| *Peak* | *P* | *80 kGy* | *P* | *80 kGy* | *P* | *80 kGy* | *P* | *80 kGy* |
| A | 21.79 | 17.90 | 100 | 100 | 28166 | 9796 | 2.60 | 2.00 |
| B | 36.00 | 36.99 | 8 | 23 | 3103 | 2281 | 0.40 | 0.30 |
| C | 42.00 | 42.00 | 4 | 7 | 3896 | 2747 | 2.90 | 0.29 |
| D | – | 72.57 | – | 15 | – | 1421 | – | 0.30 |
| E | – | 75.54 | – | 5 | – | 460 | – | 0.30 |

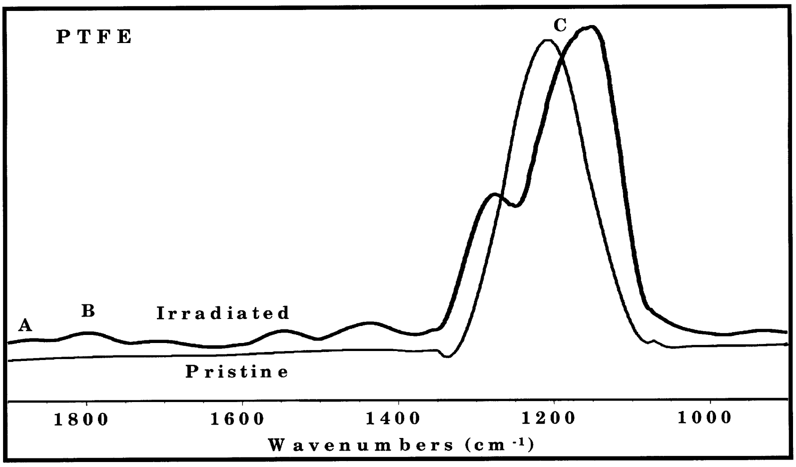


FIGURE 2 FT-IR spectra of the pristine and the proton irradiated PTFE (80 kGy) in the range of 1900–900 $\mathrm{cm}^{-1}$.

[12], these products are formed by random splitting of C—C bonds and C—F bonds to give radicals. Oxygen would add to organic radicals to give peroxy-radicals, which could react together to form alkoxy radicals as shown below.

$$-CF_2-CF_2^{\bullet}+O_2 \rightarrow -CF_2-CF_2O_2^{\bullet}$$

$$2-CF_2-CF_2O_2^{\bullet} \rightarrow 2-CF_2CF_2O^{\bullet}+O_2$$

Dissociation of alkoxy radicals produces carbonyl fluoride and a new organic radical by one $-CF_2$-unit as follows:

$$-CF_2-CF_2O^{\bullet} \rightarrow CF_2^{\bullet}+COF_2$$

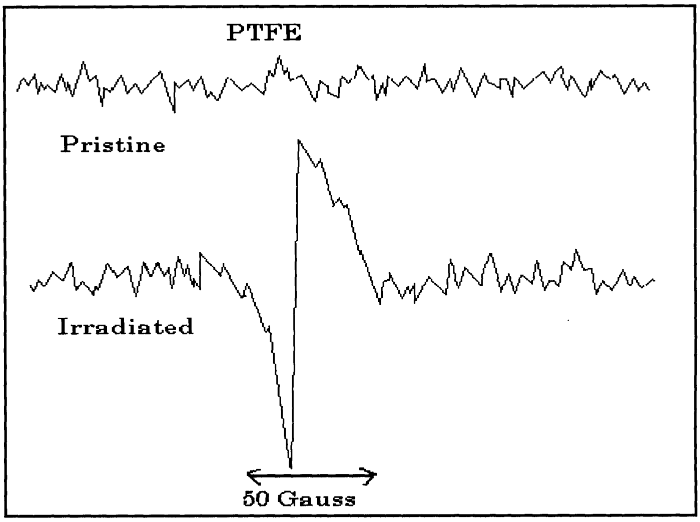


FIGURE 3 ESR spectra of the pristine and the proton irradiated PTFE (80 kGy) showing the free radical signal.

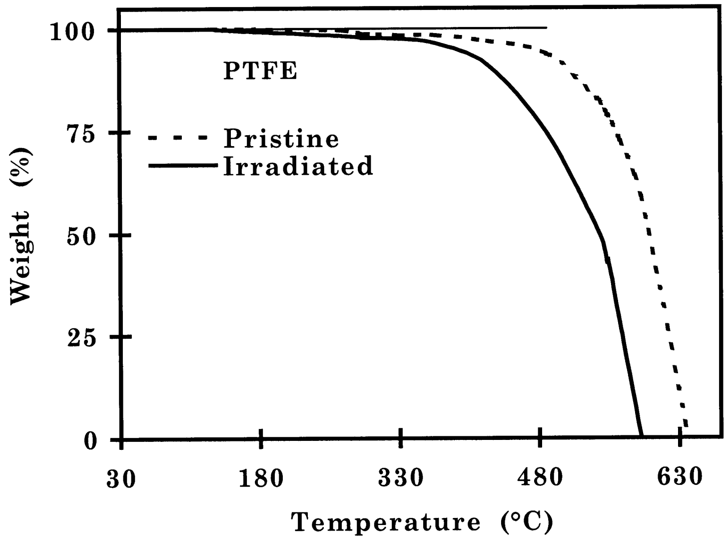


FIGURE 4 TGA thermograms of the pristine and the proton irradiated PTFE (80 kGy).

The formation of free radicals could not be traced by the ESR spectral analysis for the pristine and the irradiated PTFE at the three lower doses (10 kGy, 30 kGy and 60 kGy); the signal shows only up at the highest dose (80 kGy). Since the irradiated samples were kept at room temperature for a few months after irradiation, quite a number of free radicals formed could have been annihilated during that time. However, the PTFE sample proton-irradiated up to 80 kGy formed a relatively stable radical, which was detected by the instrument. This reveales that the proton irradiation (80 kGy) in the polymer PTFE leads to chain-scission resulting in the formation of free radicals. The increase in conductivity of the latter sample as revealed by UV-V is spectroscopy [2] is made plausible by the formation of this free radical.

## 3.4 Thermogravimetric Analysis

The TGA thermograms of the pristine and the irradiated PTFE (80 kGy) are shown in Figure 4. The thermal stability was found to decrease with the increase in proton dose. The temperature values for different decomposition zones are listed in Table II. The stable zone of decomposition was reduced from 264 °C for the pristine case to 125 °C for the PTFE sample proton-irradiated at 80 kGy. Similarly, both the slow decomposition zone (of about 5% weight loss) and the fast decomposition zone decrease with increase in proton dose.

TABLE II Thermal Decomposition Temperatures at Different Zones for the Pristine and the PTFE Samples Irradiated to Different Doses (10, 30, 60, 80 kGy) of 62 MeV Protons.

| *Dose (kGy)* | *Stable zone (°C)* | *Slow decomposition zone (°C)* | *Fast decomposition zone (°C)* |
|---|---|---|---|
| 0 | 30–264 | 264–470 | 470–639 |
| 10 | 30–257 | 257–442 | 442–631 |
| 30 | 30–244 | 244–439 | 439–625 |
| 60 | 30–157 | 157–425 | 425–613 |
| 80 | 30–125 | 125–418 | 418–607 |

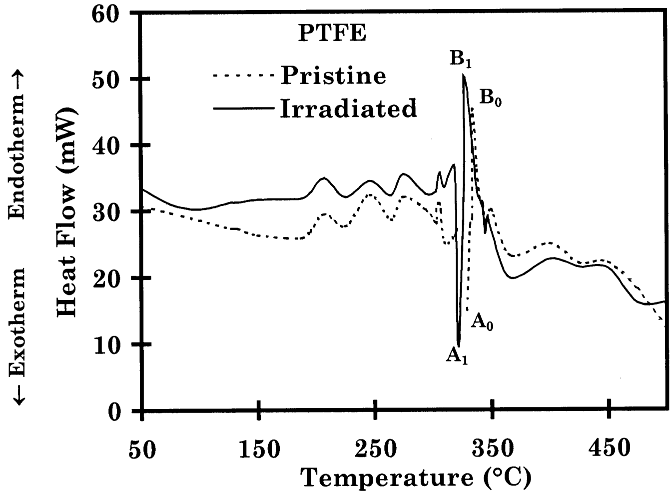


FIGURE 5 DSC thermograms of the pristine and the proton irradiated PTFE (80 kGy).

### 3.5 Differential Scanning Calorimetry

DSC analysis revealed a decrease in melting temperature of PTFE with increase in dose of proton irradiation. The DSC thermograms of the pristine and the proton irradiated PTFE (80 kGy) are shown in Figure 5. In the pristine PTFE, endothermic distortions started at around 208 °C and continued up to 330 °C ($A_0$), at which a transition from exothermic to endothermic occurred. The melting endotherm was observed at 334 °C ($B_0$). For the irradiated samples, endothermic distortions started at around 205 °C and continued up to 327 °C ($A_1$), at which a transition from exothermic to endothermic occurred. The melting temperatures gradually decreased with increase in dose and were found to be 330 °C, 328 °C, 324 °C and 321 °C ($B_1$) for the samples irradiated by 10, 30, 60 and 80 kGy, respectively. This finding is in accordance with the other studies and supports the fact that PTFE underwent chain-scission by proton irradiation.

## 4 CONCLUSION

From the results obtained by the proton irradiation (62 MeV) on PTFE, the following conclusions can be drawn.

- The decrease in the intensity of the peaks as revealed from the XRD analysis, denoted some destruction of the orderliness of the original crystal structure due to proton irradiation.
- Simultaneously, there is evidence for some radiation-induced build-up of new crystalline structures, which are, however, of marginal abundance.
- The FTIR spectra of the irradiated PTFE showed the emergence of some new peaks assigned to terminal double bonds and carbonyl stretching vibration.
- The ESR spectrum for the PTFE irradiated at the dose of 80 kGy of 62 MeV proton revealed the formation of a stable free radical.
- The thermal stability and the melting temperatures of PTFE were observed to decrease with increase in proton dose. The chain-scission induced in the polymer by proton irradiation accounts for its decomposition at low temperature.

## *Acknowledgements*

The authors thank the technical and the scientific staff of the ISL, Hahn Meitner Institute, Berlin for the proton irradiation. The fellowship grants to SPT and RM under the Senior Research Fellowship of the Council for Scientific and Industrial Research, New Delhi, India are thankfully acknowledged. KKD thanks DAAD, Bonn for the fellowship under the re-invitation programme. SG thanks DST, Government of India for the award of BOYSCAST fellowship. The authors thank the technical and scientific staff of IUC, Indore, India for their help in X-ray diffraction measurements.

## *References*

[1] Wang, G. H., Pan, G. Q., Dou, L., Yu, R. X., Zhang, T., Jiang, S. G. and Dai, Q. L. (1987). *Nucl. Instr. and Meth. B*, **27**, 410.

[2] Mishra, R., Tripathy, S. P., Sinha, D., Khathing, D. T., Dwivedi, K. K., Ghosh, S., Müller, M., Fink, D. and Chung, W. H. (2000). *Nucl. Instr. and Meth. B*, **168**, 59.

[3] Dwivedi, K. K., Ghosh, S., Fink, D., Mishra, R., Tripathy, S. P., Kulshreshtha, A. and Khathing, D. T. (1999). *Radiat. Meas.*, **31**, 127.

[4] Tripathy, S. P., Mishra, R., Kulshreshtha, A., Dwivedi, K. K., Khathing, D. T., Srivastava, A., Ghosh, S. and Fink, D. (2001). *Radiat. Meas.*, **33**, 171.

[5] Lee, E. H. (1999). *Nucl. Instr. and Meth. B*, **151**, 29.

[6] Tripathy, S. P., Mishra, R., Dwivedi, K. K., Khathing, D. T., Ghosh, S. and Fink, D. (2001). *Radiat. Meas.*, **34**, 15.

[7] Torrisi, L. and Foti, G. (1996). *J. Mater. Res.*, **5**(11), 2773.

[8] Biswas, L., Lotha, S., Fink, D., Singh, J. P., Avasthi, D. K., Yadav, B. K., Bose, S. K., Khathing, D. T. and Avasthi, A. S. M. (1999). *Nucl. Instr. Meth. B*, **159**, 40–51.

[9] Alpert, N. L., Keiser, W. E. and Szymanski, H. A. (1970). A Plenum/Rosetta edition. Published by Plenum Publishing Corporation, New York, p. 184.

[10] Schierholz, K., Lappan, U. and Lunkwitz, K. (1999). *Nucl. Instr. and Meth. B*, **151**, 232.

[11] Caro, J. C., Lappan, U. and Lunkwitz, K. (1999). *Nucl. Instr. and Meth. B*, **151**, 181.

[12] Spinks, J. W. T. and Woods, R. J. (1990). 3rd ed. Wiley Interscience Publication, p. 452.