

# Investigating the effect of heat treatment on the diffusion behaviour of xenon implanted in glassy carbon

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## Highlights

- No diffusion occurred for implanted xenon after annealing up to 800 °C.
- Diffusion occurred after annealing at 900 °C and 1000 °C.
- Implantation led to amorphization of glassy carbon in the implanted region.
- Raman spectroscopy showed slight damage annealing for annealing up to 1000 °C.

## Abstract

The effect of sequential isochronal annealing on the diffusion behavior of implanted xenon in glassy carbon is reported. Glassy carbon substrates were implanted with 200 keV xenon ions to a fluence of  $1 \times 10^{16} \text{Xe}^+ \text{cm}^{-2}$ . The sample was annealed in vacuum at temperatures ranging from 300°C to 1000 °C for 5 hours in steps of 100 °C. The RBS depth profiles obtained at temperatures above 800°C showed that some diffusion occurred. The broadening of the peaks was not accompanied with a loss of the implanted Xe. Microstructural changes in the glassy

carbon substrate due to Xe bombardment and annealing were monitored using Raman spectroscopy. The Raman spectrum obtained after xenon bombardment showed that the glassy carbon substrate became amorphised. However, a slight recovery of the glassy carbon structure was noticed after heat treatment. The SEM micrographs of the glassy carbon substrate showed an increase in the surface roughness of the glassy carbon substrate after implantation. The increase in the roughness of the glassy carbon substrate was attributed to the sputtering of the loosely bonded carbon atoms along the polishing marks after implantation and annealing.

Keywords: Diffusion; Glassy carbon; Raman spectroscopy; RBS; SEM

## **1. Introduction**

Recently, there has been an interest in employing glassy carbon to contain radioactive fission products. Glassy carbon is an apparently isotropic, continuous and non-porous material, showing conchoidal surface fracture. It is a non-graphitizing carbon which combines glassy and ceramic properties with those of graphite. Unlike graphite, glassy carbon has a fullerene-related microstructure [1]. This leads to a great variety of unique materials properties. Its high strength, high hardness and also high impermeability to gases, suggest that glassy carbon must have a unique structure different from those of regular carbons [2]. These properties allow glassy carbon to be used in a wide range of applications such as a nuclear waste storage containment material to lining of pressure vessels to acid-battery electrodes. Waste storage facilities should be designed and operated to minimize the probability and consequences of incidents and accidents. Factors that should be considered include the following: impermeability to the fission products, chemical stability against corrosion caused by processes within the waste and/or external conditions, protection against radiation damage and/or thermal damage, especially stability against the degradation of materials and resistance to impacts from operational loads or due to incidents and accidents [3].

Xenon (Xe) is a noble gas mainly produced in nuclear fission reactions. It consists of various radioactive isotopes including Xenon-135, which is of considerable significance in the operation of nuclear power reactors. Xenon-135 is a product of U-235 fission and has a very large neutron-capture cross section. This means that it acts as a neutron absorber or poison that can slow down or stop the chain reaction after a period of operation[4]. A major contribution to the sequence of events leading to the Chernobyl nuclear disaster was the failure to anticipate the effect of xenon poisoning on the rate of the nuclear fission reaction [5]. Decays radioactively with a half-life of 9.1 hours. Little of the Xe-135 results directly from fission; most comes from the decay chain, Te-135 to I-135 to Xe- 135 [6].

The aim of this paper is to investigate the diffusion behavior of implanted Xe in glassy carbon. As was mentioned above, this information is necessary to determine the effectiveness of glassy carbon as a good construction material for the casks used for nuclear waste storage. The structural changes during annealing heat treatment at different temperatures were characterised by Raman spectroscopy. Surface topographical changes due to the annealing was investigated by SEM.

## **2. Experimental procedure**

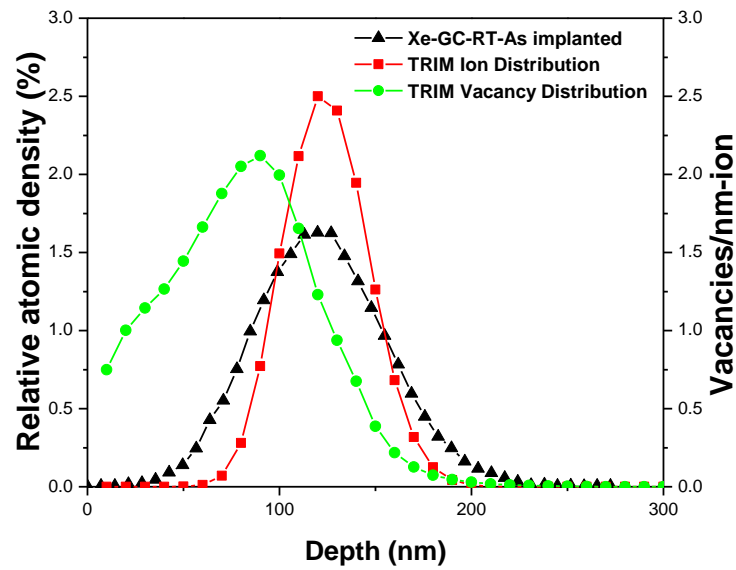
The glassy carbon (Sigradur<sup>®</sup>G) samples were polished with 1  $\mu\text{m}$  and 0.5  $\mu\text{m}$  diamond solutions respectively. The samples were implanted with 200 keV xenon ions to a fluence of  $1 \times 10^{16}$  ions/cm<sup>2</sup> at room temperature. The diffusion behavior of Xe in glassy carbon due to annealing was investigated using Rutherford backscattering spectrometry (RBS) with 1.6 MeV He<sup>+</sup> particles in a Van de Graaff accelerator. A total charge of 8  $\mu\text{C}$  was used with an analysing current of 15 nA and a scattering angle of 165°. The resulting RBS depth profiles were fitted to the solution of the Fick diffusion differential equation for an initially Gaussian implanted profile[7]. The effect of Xe implantation and annealing on the microstructure of glassy carbon

was monitored by using a Jobin Yvon, Horiba<sup>(C)</sup> TX64000 triple grating Raman spectrometer with a 514.5 nm (green) laser. The excitation laser used in this study was an Ar/Kr mixed gas laser. The 50× objective was used to acquire the Raman spectra. One of the major setbacks of Raman spectroscopy is sample heating. In order to avoid this, the laser power was kept below 1 mW at the sample during analysis.

The surface morphology of glassy carbon due to Xe implantation and annealing was investigated by using the scanning electron microscope (SEM). SEM images were obtained by using the Zeiss Ultra Plus SEM. An analysing voltage of 2 kV was used. In-lens SEM images of the sample were taken before implantation, after implantation and after every heat treatment so as to investigate all surface changes due to these treatments.

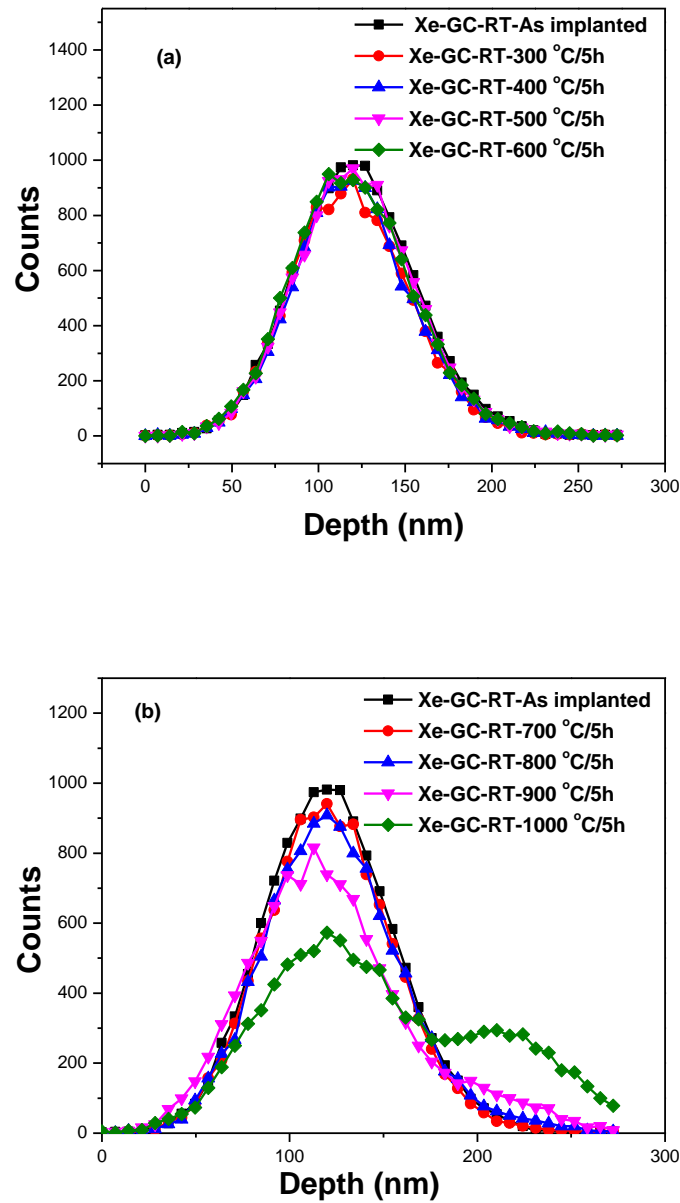
### **3. Results and discussion**

Fig. 1 shows the RBS depth profile of 200 keV xenon implanted in glassy carbon at room temperature. The profile was compared with the spectra obtained from a SRIM simulation. Fig. 1 also shows the vacancy distribution obtained from SRIM. The experimental projected range,  $R_p$ , was estimated by fitting the Xe depth profile with a Gaussian equation and the value obtained was 120 nm. This  $R_p$  value obtained for the room temperature implanted Xe depth profile is comparable to the 119 nm value obtained from SRIM. The experimental straggling,  $\Delta R_p$  value obtained is about 34 nm which is higher than the 21 nm obtained from SRIM.



*Fig. 1: RBS depth profile of 200 keV Xe<sup>+</sup> ions implanted in glassy carbon at room temperature and ion distribution profile together with vacancy distribution obtained from SRIM [8].*

Some of the implanted samples were annealed in vacuum at 300 °C -1000 °C in steps of 100 °C for 5 hours – see Fig. 2 (a) and (b). Two diffusion mechanisms can be clearly observed from the spectra shown. The first diffusion regime is between 300 °C - 800 °C. The RBS profiles obtained after annealing the samples at these temperatures showed no noticeable diffusion of the implanted Xe. The lack of diffusion at these temperatures might be due to the presence of defects in the implanted region of the glassy carbon substrate acting as traps for the implanted xenon. The diameter of Xe atom of 216 pm is much larger than the C atom of 77 pm. In Fig. 1 the SRIM vacancy distribution is compared to the implanted distribution. The  $R_{p(vac)}$  is about 79 nm which is significantly lower than the  $R_p$  value of the as-implanted Xe depth profile (120 nm). This discrepancy implies that the defects introduced into the glassy carbon substrate are concentrated towards the surface. The fact that the Xe atoms deeper inside the glassy carbon also did not diffuse indicates that the concentration of the vacancies was enough to trap the (also fewer) Xe atoms.



*Fig. 2. RBS Depth profiles of Xe implanted at room temperature after isochronal annealing at (a) 300 °C - 600 °C for 5 h and (b) 700 °C - 1000 °C for 5 h.*

In the second diffusion regime (900 °C - 1000 °C), movement of Xe into the bulk of the glassy carbon was observed with the formation of a bimodal distribution. The migration of Xe into the glassy carbon was accelerated at 1000 °C with a new Xe peak formed within the bulk of the glassy carbon. The movement of Xe deeper inside the glassy carbon substrate was not accompanied with a diffusion of Xe towards the surface of glassy carbon. This suggests that a Fickian type of diffusion is not responsible for the diffusion observed in this regime.

Odutemowo et al. [9] studied the diffusion of strontium in glassy carbon and observed a related phenomenon when they annealed their Sr implanted glassy carbon samples at high temperatures. They observed segregation of Sr towards the surface of glassy carbon instead of towards the bulk as seen in our results.

In order to estimate the diffusion coefficient of Xe in glassy carbon, the RBS depth profiles obtained at 300 – 800 °C were fitted to the solution of the Fick diffusion equation with originally a Gaussian profile and with a perfect sink at the surface [7]. Examples of such fits are shown in Fig. 3. The fitting of the RBS spectra shows that the diffusion coefficient of Xe in glassy carbon could not be estimated. This is in agreement with the results discussed earlier (no noticeable diffusion of Xe was observed).

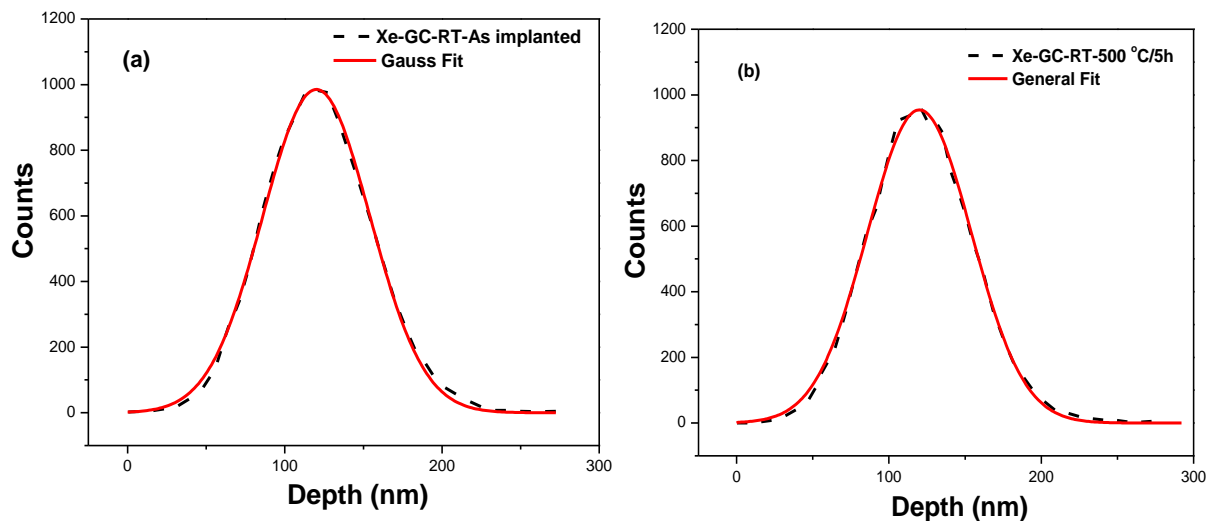
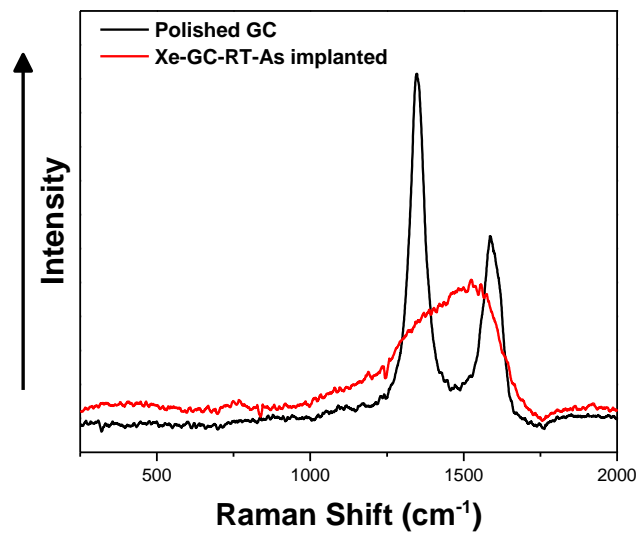


Fig. 3: The diffusion solution for a Gaussian implanted profile fitted to the RBS spectra of the samples (a) implanted at RT, (b) annealed at 500 °C.

Fig.4. shows the Raman spectra measured for the pristine glassy carbon and Xe-implanted glassy carbon. The pristine glassy carbon sample shows two pronounced peaks: the D peak at  $1350\text{ cm}^{-1}$  the G peak at  $1588\text{ cm}^{-1}$ , in line with many other investigations [9-12]. The G peak originates from the  $\text{sp}^2$  vibrations of graphite while the D peak from disordered  $\text{sp}^3$  bonds.

These two peaks of the glassy carbon indicate the presence of small graphitic crystallites (ribbons) imbedded in the amorphous matrix. After implantation the peaks merged into a single broad band indicating amorphisation of these graphitic crystallites. This result is in agreement with what has been reported for several  $sp^2$  carbon materials [9-14].

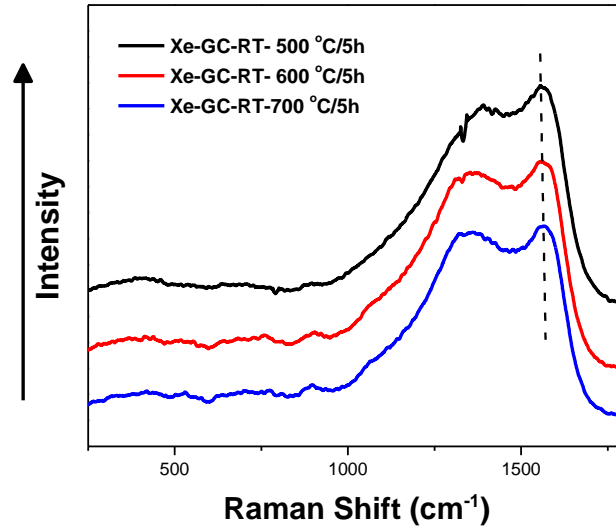


*Fig.4: Raman spectrum of glassy carbon before and after Xe bombardment.*

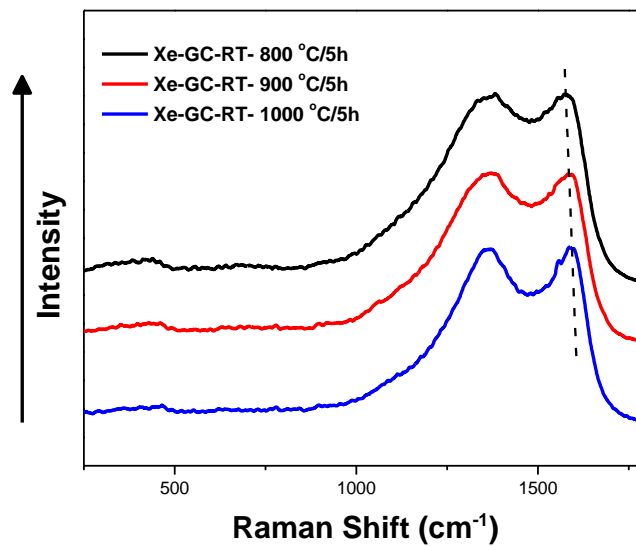
Fig. 5 (a) and (b) show the effect of isochronal heat treatment on the glassy carbon structure. This was done by annealing the implanted samples at temperatures ranging from 500 °C to 700 °C for 5 hours in vacuo. The Raman spectra in Fig. 5 showed the appearance of small D and G peaks indicating a slight annealing of the radiation damage of the glassy carbon. The annealing effect enhanced with increasing annealing temperature indicated by the increase in these two Raman peaks. However, the structure does not return to that of the pristine glassy carbon. Odutemowo et al. [12] found that recovery of the radiation damage only occurred after annealing at much higher temperatures than in the present study. Only after annealing



strontium implanted glassy carbon at 2000 °C for 5 h did they obtain a typical Raman spectrum for glassy carbon.



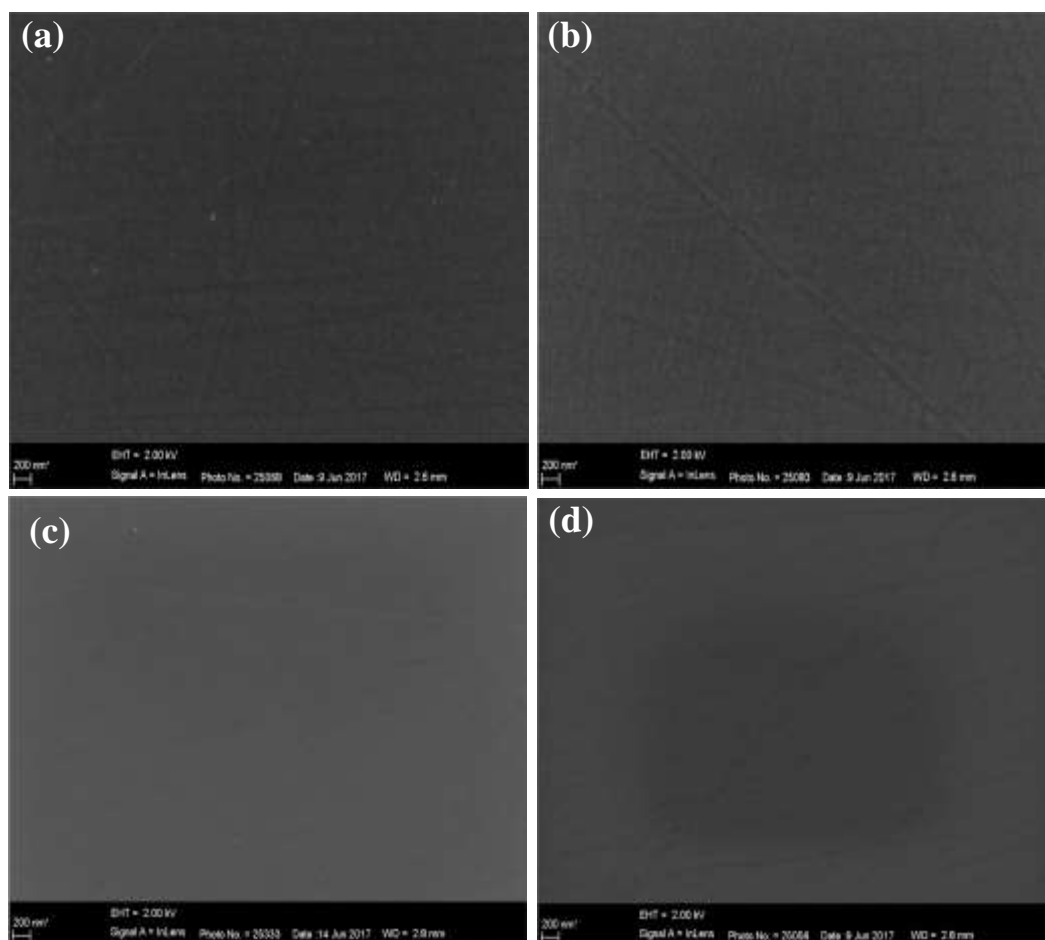
*Fig. 5 a: Raman spectrum of Xe implanted glassy carbon after annealing at 500°C-700°C.*



*Fig.5 b: Raman spectrum of Xe implanted glassy carbon after annealing at 800°C-1000°C.*

Fig.6 (a), (b), (c) and (d) show the SEM micrographs obtained before and after Xe implantation. The SEM images show that the polishing marks became more prominent after Xe implantation. The prominence of the polishing marks after Xe implantation is as result of the increased

sputtering of the carbon atoms in the vicinity of the polishing marks. Due to the strain in the material at these regions, the surface atoms have less binding energies than the pristine surface regions and, consequently sputter more easily, thereby exposing the polishing lines. The effect of high temperature annealing is shown in Fig.6 (c) and (d). Annealing of the implanted sample at 1000 °C resulted in a smoother surface with the polishing marks less visible. The reduction in the surface topography at this temperature is due to the enhanced surface diffusion (see Fig.6(c)) leading to a smoothing effect on the surface of the glassy carbon substrate.



*Fig. 6. SEM micrographs of (a) the pristine glassy carbon, (b) as-implanted Xe glassy carbon, (c) 900 °C and (d) 1000 °C for 5 h annealed in vacuum.*

#### **4. Conclusion**

The diffusion behavior of Xe in glassy carbon was investigated using Rutherford backscattering spectrometry (RBS). RBS depth profiles obtained after annealing the sample at 300 °C – 800 °C showed that there was no diffusion of the implanted Xe into the bulk or towards the surface of glassy carbon. This non-diffusion was attributed to the presence of defect traps acting as a diffusion barrier in the glassy carbon. At the highest annealing temperatures (900 °C – 1000 °C), there was a movement of Xe into the bulk of the glassy carbon with a new peak formed within the glassy carbon bulk. However, the movement of Xe was limited to the damaged region, which suggests that glassy carbon is a good containment material for xenon. The Raman spectra obtained after Xe implantation shows that the implanted layer of the glassy carbon became amorphized. Annealing of the sample to 1000 °C only resulted in the partial recovery of the glassy carbon structure. The SEM results show that implantation and subsequent annealing did not have any major effects on the surface topography of the glassy carbon substrate.

#### **Acknowledgement**

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#### **References**

- [1] T. Noda, M. Inagaki, and S. Yamada, “A Comment on the Structure of Glassy Carbon,” *Bulletin of the Chemical Society of Japan*, vol. 41, no. 12. pp. 3023–3024, 1968.
- [2] SPI Supplies, “Glassy Carbon Product Information,” pp. 1–5, 2009.
- [3] H. Krause, “Storage of radioactive waste,” *Naturwissenschaften*, vol. 59, no. 9, pp.

412–417, 1972.

- [4] John Wiley & Sons, Ltd “*Radionuclides in the Environment*”. 2010. ISBN 978-0-470-71434-8
- [5] E. Physics, “Xenon Effects on Nuclear Reactor Reactivity,” pp. 1–6, 2003.
- [6] P. L. Roggenkamp, “The Influence of Xenon-135 on Reactor Operation,” pp. 49–56, 2000.
- [7] J.B. Malherbe, P.A. Selyshchev, O.S. Odutemowo, C.C. Theron, E.G. Njoroge, D.F. Langa, T.T. Hlatshwayo, Diffusion of a mono-energetic implanted species with a Gaussian profile, *Nucl. Instrum. Methods Rel. Phys.* (2016) 406 (2017) 708-713.
- [8] J. Ziegler, SRIM 2012 computer code, (2012). [www.srim.org](http://www.srim.org).accessed May 24, 2017.
- [9] O. S. Odutemowo, J. B. Malherbe, C. C. Theron, E. G. Njoroge, and E. Wendler, “In-situ RBS studies of strontium implanted glassy carbon,” *Vacuum*, vol. 126, no. March, pp. 101–105, 2016.
- [10] D. McCulloch, S. Praver, and A. Hoffman, “Structural investigations of xenon-ion-beam-irradiated glassy carbon,” *Phys. Rev. B* 50 (1994) 5905-5917.
- [11] T. T. Hlatshwayo, L. D. Sebitla, E. G. Njoroge, M. Mlambo, and J. B. Malherbe, “Annealing effects on the migration of ion-implanted cadmium in glassy carbon,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 395, pp. 34–38, 2017.
- [12] O.S. Odutemowo, J.B. Malherbe, L. Prinsloo, D.F. Langa and E Wendler, “High temperature annealing studies of strontium ion implanted glassy carbon”, *Nucl.Instrum. Methods Phys. Res. B* 371 (2016) 332-335
- [13] K. Niwase, T. Tanabe, I. Tanaka, " Annealing experiment of ion-irradiated graphite by laser Raman spectroscopy," *Journal of Nuclear Materials* 191 (1992) 335-339.
- [14] K. Niwase, "Irradiation-induced amorphization of graphite," *Physical Review B* 52 (1995) 15785-15798.