

Effect of heat treatment on the migration behaviour of Sr and Ag CO-implanted in glassy carbon

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Highlights

- Ag implanted glassy carbon was vacuum annealed at 400 °C - 700 °C for 1 h.
- Fickian diffusion of Ag was observed at high annealing temperatures.
- Glassy carbon samples were co-implanted with Ag and Sr and then annealed.
- The RBS depth profile showed that the introduction of Sr into the glassy carbon matrix only slightly affect the diffusion behaviour of Ag in Sr.
- The diffusion behaviour of Sr on the other hand was majorly affected by the presence of Ag in the glassy carbon.

Abstract

The effect of annealing on the diffusion of silver, silver and strontium co-implanted in glassy carbon was investigated. Glassy carbon samples were implanted with 360 keV Ag ions at room temperature. The RBS profile showed that Fickian diffusion of Ag in glassy carbon is only observed at temperatures ranging from 500 °C–600 °C. At higher annealing temperatures, there was a significant loss of Ag and no Ag was retained in glassy carbon at 700 °C. Glassy carbon samples were also co-implanted with Ag and Sr. The diffusion behaviour of Ag when co-implanted with Sr was similar to that of the singly implanted Ag sample. However, the introduction of Sr into the glassy carbon matrix assisted in the retainment of the Ag ions. The co-implantation of Ag and Sr resulted in a change in the diffusion behaviour of Sr in glassy carbon. The implantation of Ag with Sr prevented the movement of Sr deeper into the bulk of the glassy carbon. The non-movement of Sr into the bulk of the glassy carbon was attributed to the increase of radiation damage near the surface of the glassy carbon making diffusion of Sr towards the surface of glassy carbon an easier choice.

Keywords: Annealing; Diffusion; Glassy Carbon; Rutherford Back-scattering Spectrometry; Co-implantation

1. Introduction

Recently, there has been a prediction of a nuclear renaissance over the next years [1]. Stakeholders are predicting a possible tripling of nuclear usage by 2050 [2]. This renewed interest can be attributed to the Paris agreement signed in 2016 [3]. The need to limit the global temperature increase to below 2 °C and to checkmate the ever rising energy and hydrocarbon oil prices have made nuclear power once again a proposed alternative source of power generation [2,4,5]. Stakeholders have agreed that the nuclear industry must first resolve the significant economic, safety, security and waste disposal challenges that have plagued its development for several years [2,6]. One of the major challenges faced by the nuclear industry is the problem of proper waste storage and management. High level nuclear wastes (HLW), i.e. wastes generated by nuclear reactors, are known to be extremely toxic to living organisms when they are exposed to it. With the resurgence of nuclear power, the quantity of nuclear waste generated is expected to increase significantly in the coming years. There have been several studies that aim to propose better methods of storing HLWs especially for long term storage [7,8]. Recently, it was proposed that glassy carbon could be an alternative material from which the storage containers could be manufactured [11]. This study aims to further investigate this proposal by looking at the migration of Sr and Ag in glassy carbon.

Glassy carbon (vitreous carbon) is non-graphitising carbon with a fullerene related structure [9]. It is a sp^2 carbon that does not graphitize at temperatures up to 3000 °C. Its high stability, strength, hardness and corrosion resistance are some of the properties that make glassy carbon a possible candidate for HLWs storage.

Sr-90, an isotope of strontium is considered to be one of the most toxic constituents of HLWs. It has the ability to replace calcium in the bones eventually causing cancer if the level of exposure is left uncontained. Ag-110 is also another dangerous fission product because of its half-life of 253 days. Exposure to this isotope may lead to health problems including kidney and liver malfunction [10].

Due to the hazardous nature of Sr-90, we previously investigated the diffusion behaviour of strontium in glassy carbon [[11], [12], [13]]. The most notable finding in our previous study is the movement of the implanted Sr into the bulk of the glassy carbon substrate at low temperature. This migration was attributed to the redistribution of the defects introduced into the glassy carbon during implantation. The segregation and loss of Sr at high annealing temperatures was also observed.

In this work, the diffusion behaviour of Ag singly implanted in glassy carbon was investigated by using Rutherford backscattering spectrometry (RBS). Because of the RBS results of the Ag implanted glassy carbon samples, some of the glassy carbon samples were also co-implanted with Sr and Ag ions at room temperature. This was done in order to investigate the effect of Ag on the diffusion behaviour of Sr in glassy carbon.

1.1. Experimental procedure

Two different sets of samples were prepared. In the first set, glassy carbon samples were implanted with 360 keV Ag ions to a fluence of 2×10^{16} ions/cm² at room temperature. The Ag implanted samples were annealed isochronally in vacuum at temperatures ranging from 400 °C–700 °C for 1h. The migration behaviour of the implanted Ag in glassy carbon after annealing was investigated by using Rutherford backscattering spectrometry (RBS) with 1.6 MeV He⁺ in a van der Graaff accelerator. A total charge of 8 µC and a scattering angle of 165° was used for analysis.

In the second set of samples, glassy carbon substrates were first implanted with 200 keV silver and then also with 200 keV strontium ions to a fluence of 1×10^{16} ions/cm² at room temperature. The implanted samples were annealed isochronally in vacuum at temperatures ranging from 300 °C to 1000 °C for 1h in steps of 100 °C. The diffusion behaviour of Sr/Ag in glassy carbon due to heat treatment was studied by using Rutherford backscattering spectroscopy (RBS) with 2.5 MeV He⁺ in a tandem accelerator. A total charge of 14 µC and a scattering angle of 168° was used for analysis. Because the effect of radiation damage due to implantation was of interest during the study, the flux during all implantation was kept at about 10^{13} cm⁻²s⁻¹. This was done to avoid an increase in the glassy carbon substrate temperature.

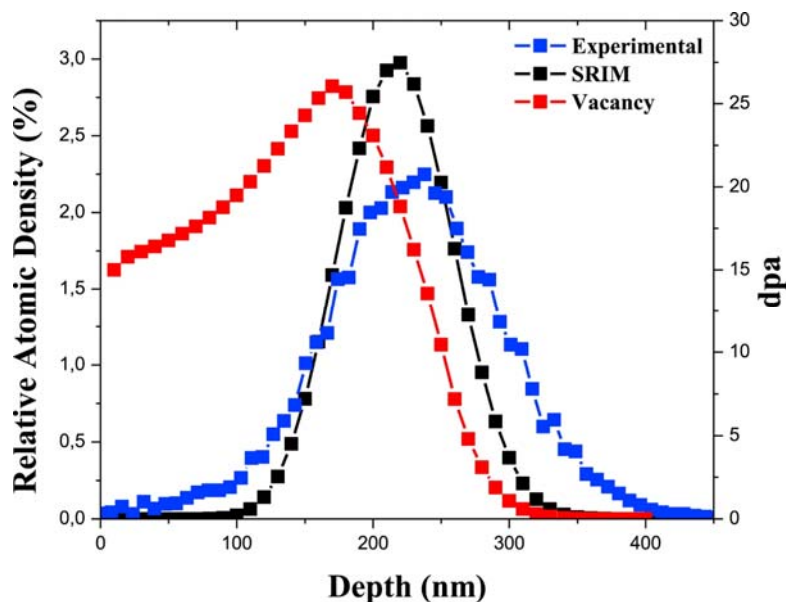


Fig. 1. The RBS determined depth profile (blue curve) of 360 keV Ag⁺ implanted into glassy carbon is compared with a SRIM simulation (black curve). The vacancy distribution (red curve) as calculated by SRIM is also shown.

2. Results and discussion

Fig. 1 shows the 360 keV implanted Ag RBS experimental depth profile. The RBS depth profile was compared with that obtained by SRIM. The SRIM simulation was done by taking the density of glassy carbon as 1.42 g/cm³. The RBS profile was converted into a depth profile by also using 1.42 g/cm³ as the density of glassy carbon. The RBS depth profile was

fitted with an Edgeworth equation to obtain the first four moments namely; projected range (R_p), straggling (ΔR_p), kurtosis (β) and skewness (γ). The experimental projected range is slightly lesser than that predicted by SRIM. However, it is within the error limits of both the SRIM program and the RBS depth scale.

A comparison of all the moments acquired experimentally to those predicted by SRIM is shown in Table 1. The straggling, ΔR_p , obtained experimentally is larger than that predicted by SRIM. Although the difference is near the two (i.e. SRIM and RBS) error limits, there might also be a contribution by the change in the density of the glassy carbon substrate during implantation. It has been reported [14] that ion implantation leads to a densification of glassy carbon from 1.42 g/cc to 2.03 g/cc for 200 keV strontium ions. At the lower substrate densities, the Ag ions will penetrate deeper into the glassy carbon while at the higher densities there will be a shallower profile. The combined effect was then a broader profile with a large value for ΔR_p . The experimental third (skewness) and fourth (kurtosis) moments are reasonably close to those predicted by SRIM. They also indicate that implanted Ag profile is very near to a Gaussian. (For a Gaussian profile $\beta = 3$ and $\gamma = 0$.)

Table 1. The experimental and the theoretical (SRIM) range parameters.

	EXPERIMENTAL	SRIM
IONS PROJECTED RANGE (R_p)	208.6 nm	210.56 nm
STRAGGLING (ΔR_p)	53.40 nm	40.20 nm
SKEWNESS (γ)	0.1107 nm	0.0631
KURTOSIS (β)	2.98	2.8346
PEAK POSITION OF THE VACANCY DISTRIBUTION		~170 nm

Also shown in Fig. 1 is the SRIM predicted vacancy distribution. From the figure, it can be clearly seen that the peak of the vacancy distribution is about 40 nm less than that of SRIM projected range and is skewed towards the surface. This is due to the nature of the energy loss mechanisms.

It is known that the diffusion of an impurity critically depends on the microstructure of the substrate usually enhancing diffusion and in some cases even inducing diffusion [15]. Since ion implantation can cause radiation damage with significant changes to the microstructure of a substrate [16] the damage profile in dpa in the glassy carbon as a result of Ag implantation is also given in Fig. 1. The dpa values for the Ag implantation are significantly higher than for the Sr implantation which will be discussed later in the paper.

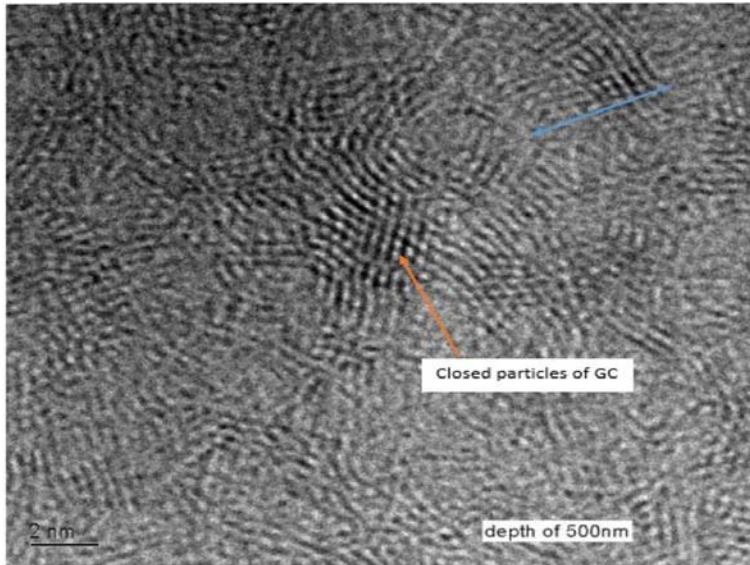


Fig. 2. HRTEM micrograph of pristine glassy carbon. Taken from Ref. [11].

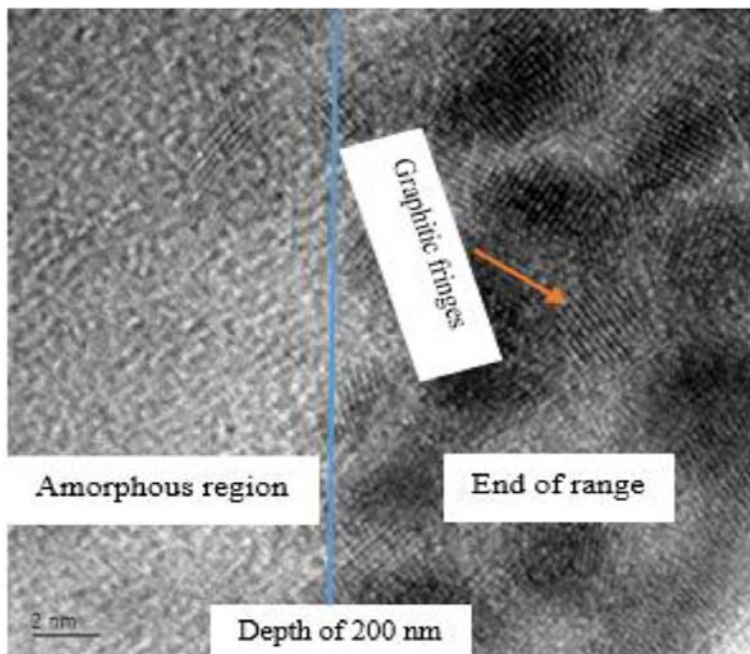


Fig. 3. HRTEM micrograph showing the effect of Sr bombardment at a depth of 200 nm in glassy carbon. Taken from Ref. [11].

The current accepted model of the microstructure of glassy carbon is that of very small curved and interlinked graphite sheets in a largely amorphous matrix [9,11]. In a recent study by Odutemowo et al. [11], high resolution TEM investigations confirmed the fullerene structure of the graphite sheet model by Harris [9] – see Fig. 2. It also showed (see Fig. 3) that 200 keV Sr implantation to a fluence of $1 \times 10^{16} \text{ Sr}^+/\text{cm}^2$ (the same as used in the present study) in glassy carbon led to amorphisation of the substrate. Thus, one can expect that the co-implantation of the heavier Ag to a fluence twice that of Sr will definitely result an amorphisation of the glassy carbon substrate used in the present study. Annealing done

for the diffusion studies will slightly alter the microstructure of annealed pre-ion bombarded glassy carbon [[11], [12], [13]]. A recent study [17] indicated that the amorphous carbon recrystallised as small graphite crystallites. Even vacuum annealing at 2000 °C did not lead to a recovery of the glassy carbon microstructure in the amorphised layer but only to graphite crystallites. The graphite crystallites slightly increased in size with increasing annealing temperature. The average size was of the same order of magnitude as that of the pristine glassy carbon.

The RBS Ag depth profiles of the as-implanted and annealed glassy carbon samples are presented in Fig. 4. The profiles were fitted to a Gaussian function and the results are presented in Table 2. Included in this table are the amount of the retained Ag ions after annealing at different temperatures. The amount of retained Ag ions was derived by adding up the number of Ag counts obtained from the Ag profile after implantation. The number of as-implanted Ag counts were then compared to the Ag counts obtained after each annealing temperature.

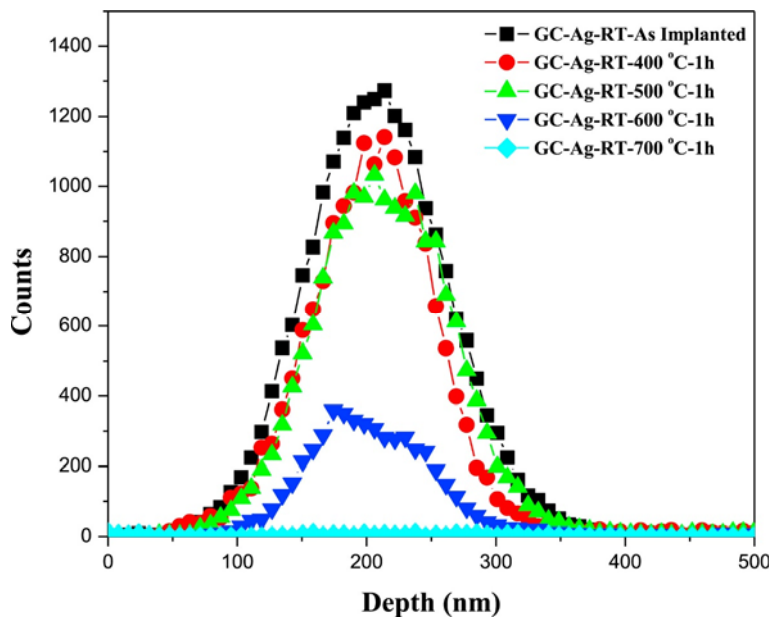


Fig. 4. RBS depth profiles of Ag singly implanted in glassy carbon and then sequentially annealed in vacuum from temperatures of 400 °C–700 °C for 1 h.

Table 2. A comparison of the range parameters obtained from fitting a Gauss function to the experimental Ag profiles after vacuum annealing for 1 h at the temperatures indicated in the table. Also shown is the normalised area under each profile.

Parameter	30 °C	400 °C	500 °C	600 °C
Projected Range R_p (nm)	207.1	205.7	212.4	199
Range Straggling ΔR_p (nm)	53.58	46.6	52.2	46.6
Retained Ions (%)	100	79.5	78	24

Annealing the sample at 400 °C resulted in a slight reduction of height and width of the Ag profile. This reduction suggests that there was a slight loss of the Ag, which is confirmed in

Table 2 by the reduction in the normalised area under the Ag profile. The reduction of the Ag peak height as well as the reduction of the straggling, ΔR_p , suggests that the diffusion mechanism of Ag in glassy carbon is not Fickian. Annealing of the implanted sample at 500 °C resulted in a slight broadening of the Ag profile. The Gaussian fit to the graph shows an increase in the ΔR_p , when compared with the 400 °C annealed sample. The broadening of the Ag profile after annealing at 500 °C suggests that Fickian diffusion of Ag in glassy carbon occurred at this temperature. It was possible to extract the diffusion coefficient of Ag in glassy carbon at 500 °C using the method described in Ref. [18] and will be discussed below. The diffusion was accompanied with a slight loss of Ag. The normalised area showed a 22% loss of the implanted Ag. The RBS depth profile obtained after annealing the sample at 600 °C showed that the Ag peak height and width reduced drastically. These reductions showed that there was a significant loss of Ag after annealing at 600 °C – see Fig. 4 and Table 2. The increase in the loss of Ag at 600 °C can be attributed to the increased mobility of vacancies and interstitial introduced during the implantation process. Interstitials and vacancies become mobile at high temperature leading to re-arrangement in the local bonding and the graphite-like crystallites with the defect region growing in size. The re-arrangement of the glassy carbon crystallites may lead to increased mobility of the implanted Ag ions [19]. Annealing at 700 °C resulted in total loss of the implanted Ag from the glassy carbon substrate.

As discussed above, the RBS depth profile obtained after annealing the implanted samples at 500 °C showed a slight broadening, i.e. increase in ΔR_p . However, after annealing at 600 °C, there was a slight reduction in the width of the Ag profile. Consequently, some samples were annealed at temperatures between 500 and 600 °C to extract diffusion coefficients at these temperatures. One sample was also isothermally annealed at 575 °C for 2, 4 and 8 h in vacuum. The Ag profiles are shown in Fig. 5. The method to determine the diffusion coefficient is discussed in Ref. [20].

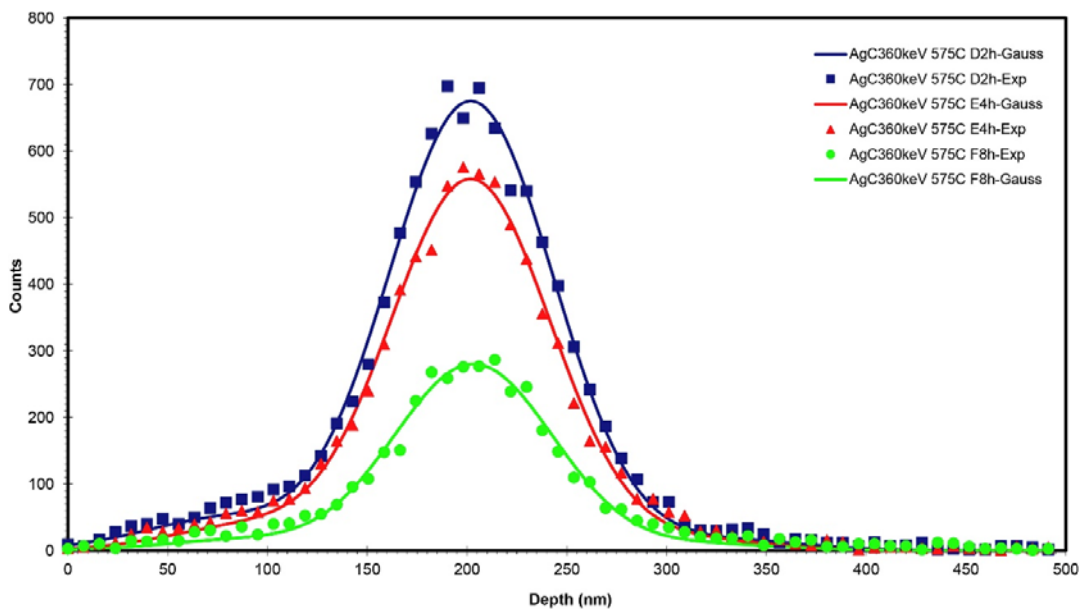


Fig. 5. Depth profiles of 360 keV silver ions implanted to a fluence of 2×10^{16} Ag⁺/cm² into glassy carbon at room temperature, and then isothermally annealed at 575 °C for 2 (blue squares), 4 (red triangle), and 8 h (green solid cycles). Gaussian fits of the profiles are also shown by the solid curves.

From Table 3, it can be seen that diffusion coefficients did not follow the normal trend where the diffusion coefficient increases with increasing temperature. Only the two isothermally annealed samples followed this trend while the diffusion coefficient for the isochronally annealed sample was higher even for a lower annealing temperature. The reason for this seemingly discrepancy is due to the difference in the microstructure of the two sets of samples. Raman spectroscopy analysis of glassy carbon implanted with other species [11,21] has shown that the glassy carbon substrate is significantly damaged after ion bombardment. Annealing of these samples at the same temperatures used in this study showed some, albeit limited recovery of the radiation damage. In both sets of samples, the implantation of 360 keV Ag introduced radiation damage in the glassy carbon samples in the near surface region of the glassy carbon. Annealing using different conditions, will lead to differences in the annealing of the radiation damage, and, consequently, to a different microstructure of the glassy carbon in the implanted regions for the two sets of samples. Impurity diffusion in a particular substrate is strongly dependent on the microstructure of the substrate.

Table 3. Diffusion coefficients for 360 keV silver in glassy carbon.

Temperature (°C)	Diffusion coefficient D (m ² /s)
500	7.7×10^{-20}
550	3.7×10^{-20}
575	5.3×10^{-20}

Another interesting aspect of the Fickian diffusion of implanted silver in glassy is the very limited temperature range in which this diffusion occurred – only from about 500 °C to 575 °C. An isothermally annealed sample at 585 °C showed no broadening of the implanted Ag profile. As can be seen from Table 2 isochronal annealing at 600 °C even led to a narrowing of the Ag profile.

We have previously investigated the migration behaviour of Sr in glassy carbon [9,10]. To do this, glassy carbon samples were implanted with 200 keV Sr ions at room temperature to a fluence of 1×10^{16} ions/cm². Annealing the implanted sample at low temperatures resulted in the movement of Sr deeper into the bulk of the glassy carbon sample. Due to this observation, Ag was co-implanted with Sr in glassy carbon and the effect of Ag on the diffusion behaviour of Sr was investigated using RBS.

The RBS depth profile of Sr and Ag co-implanted in glassy carbon is shown in Fig. 6. The RBS profiles were plotted as a function of channel number to show the overlapping of the Sr and Ag peaks. The peak present at channel 190 is sulphur which was also present in the pristine glassy carbon samples. Also shown are the RBS profiles obtained after annealing the sample at 300 °C and 400 °C respectively.

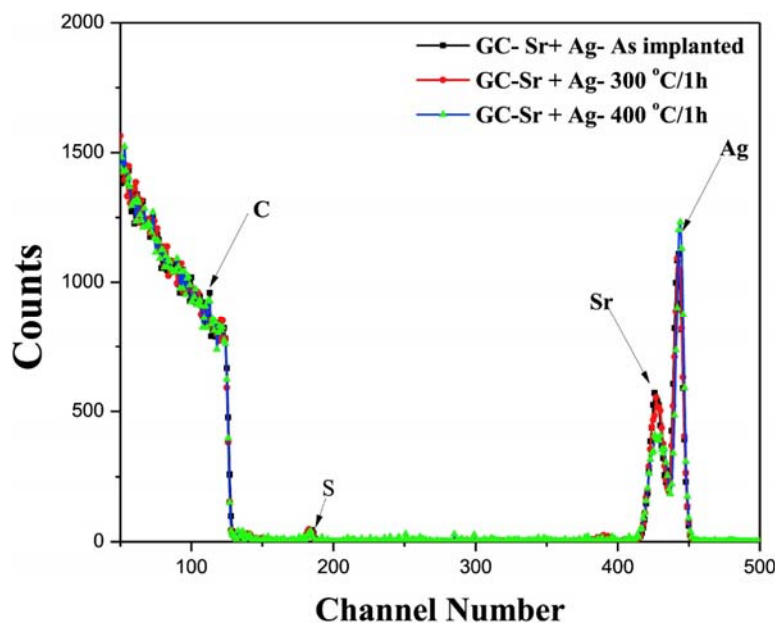


Fig. 6. RBS profile showing the carbon, strontium and silver peaks.

The as-implanted Sr and Ag profiles have been split so that they can be compared with those obtained from a SRIM simulation – see Fig. 7. The SRIM and RBS depth profiles were obtained by taking the density of the glassy carbon as 1.42 g/cm³ and not the usual 2.4 g/cm³ for graphite [22]. Fig. 7a compares the experimental depth profile of the implanted Sr with that predicted by SRIM. Also shown in the Fig. is the SRIM predicted vacancy distribution. Similarly to 360 keV Ag implanted into glassy carbon, the damage introduced by Sr is predicted by SRIM to be concentrated nearer to the surface than the Sr depth profile and also skewed towards the surface. The radiation damage profile suggests that the diffusion of Sr will be towards the surface of glassy carbon. This is due to the increased damage (vacancies, interstitials, voids, etc.) towards the surface of the glassy carbon substrate.

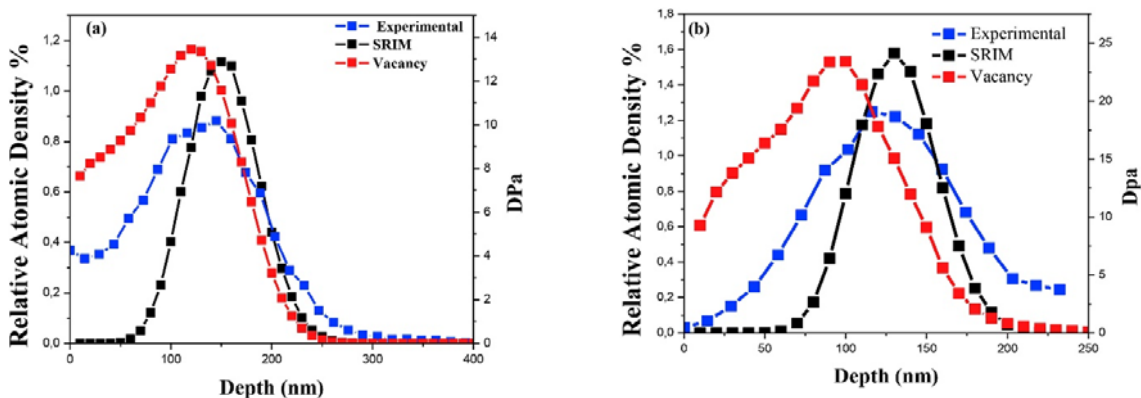


Fig. 7. As-implanted depth profiles of (a) Sr and (b) Ag compared with SRIM simulations. Also shown in the figures are the Ag and Sr vacancy distributions.

The experimental Ag profile was also compared with that obtained from SRIM as shown in Fig. 7b. The figure also shows the SRIM predicted vacancy distribution. SRIM also predicts

that a large portion of the Ag damage profile is concentrated towards the surface of the glassy carbon substrate. Another key feature shown in Fig. 7b is that the maximum height of Ag vacancy distribution profile is higher than maximum height of the Sr vacancy distribution profile. This implies that the implantation of Ag in glassy carbon introduced more damage (vacancies) into the glassy carbon matrix.

The Sr and Ag as-implanted profiles were fitted with an Edgeworth distribution equation to obtain the first four moments as shown in Table 4. The density of glassy carbon was taken as 1.42 g/cm³ for both the SRIM simulation and RBS analysis. For the Sr implantation, SRIM predicted the projected range, R_p , that is significantly higher (about 20%) than what was obtained from the experimental depth profile. The straggling, ΔR_p , obtained experimentally is also significantly higher than the SRIM prediction. The discrepancies in the result could be as a result of the change in the microstructure of glassy carbon due to the initial Ag implantation. This change in the microstructure will essentially lead to an increase in the density of the implanted glassy carbon layer and this may affect the accuracy of the SRIM simulations. The kurtosis, β , and skewness, γ , values obtained from SRIM and experimentally show that the SRIM and experimental profiles are nearly Gaussian.

Also shown in Table 4 are the first 4 moments of the Ag profile as predicted by SRIM and those obtained experimentally. The projected range, R_p obtained by SRIM is very comparable to what was obtained by fitting the as-implanted Ag profile. However, the ΔR_p predicted by SRIM is significantly lesser than that obtained experimentally. The reasons for the discrepancy in the straggling, ΔR_p , obtained experimentally and from SRIM have already been given for the 360 keV Ag implanted sample. The fluence of the implanted Ag samples was half that of the singly implanted samples. This means that the increase in glassy carbon density during implantation would play a greater role in the discrepancy between the SRIM and experimental ΔR_p in the dual implanted samples than in the singly Ag implanted samples.

Table 4. A comparison of the first four moments of the experimental and SRIM simulated profiles. The silver and strontium experimental profiles were fitted to the Edgeworth function.

Parameter	Ag Experiment	Ag SRIM	Sr Experiment	Sr SRIM
Projected Range, R_p (nm)	124	126.5	127	157
Range Straggling, ΔR_p (nm)	46.2	24.7	64.6	34.5
Skewness, γ	-0.00032	0.1485	-0.0802	0.015
Kurtosis, β	3	2.869	2.999	3

The RBS depth profiles in Fig. 8 show the effect of annealing at different temperatures on the implanted Ag. The implanted samples were annealed in vacuum at temperatures ranging from 300 °C to 700 °C for 1h. At 300 °C, there was no noticeable broadening of the Ag peak. This indicates that there was no diffusion of the implanted Ag in glassy carbon at this temperature. There are two possible reasons for the non-diffusion of Ag at 300 °C. The activation energy of diffusion is considerably higher than the average kinetic energy of the Ag ions at this temperature. It could also be attributed to the trapping of the implanted Ag in the vacancies and interstitials introduced in the glassy carbon during implantation. Studies have shown that vacancies and interstitials are generally immobile in glassy carbon

at low temperatures, however, they may become mobile at higher temperatures [23]. A general trend of a slight shift of the Ag peak towards the surface of the glassy carbon with increasing annealing temperature was observed. This is reflected by the projected range values in Table 5. The shift in the Ag profile was accompanied by a slight reduction in the ΔR_p . The reduction in ΔR_p at these temperatures indicate that the diffusion observed is not Fickian. As can be seen in Table 4 there was a slight broadening of the RBS profile of the 600 °C profile compared to the 500 °C profile. As discussed above, the 360 keV Ag implanted samples also exhibited some Fickian diffusion in this temperature range. This indicates that there was some Fickian diffusion taking place during the vacuum annealing at 600 °C. The amount of retained Ag ions at 600 °C was estimated by calculating the normalised areas (to the area under the as-implanted profile) under the Ag profiles. The normalised area was calculated by using the equation:

$$I = \int_0^{\infty} A \exp\left(-\frac{(x-R_p)^2}{2\Delta R_p^2}\right) dx = A\Delta R_p \sqrt{\frac{\pi}{2}} \cdot \text{erf}\left(\frac{R_p}{\sqrt{2}\cdot\Delta R_p}\right)$$

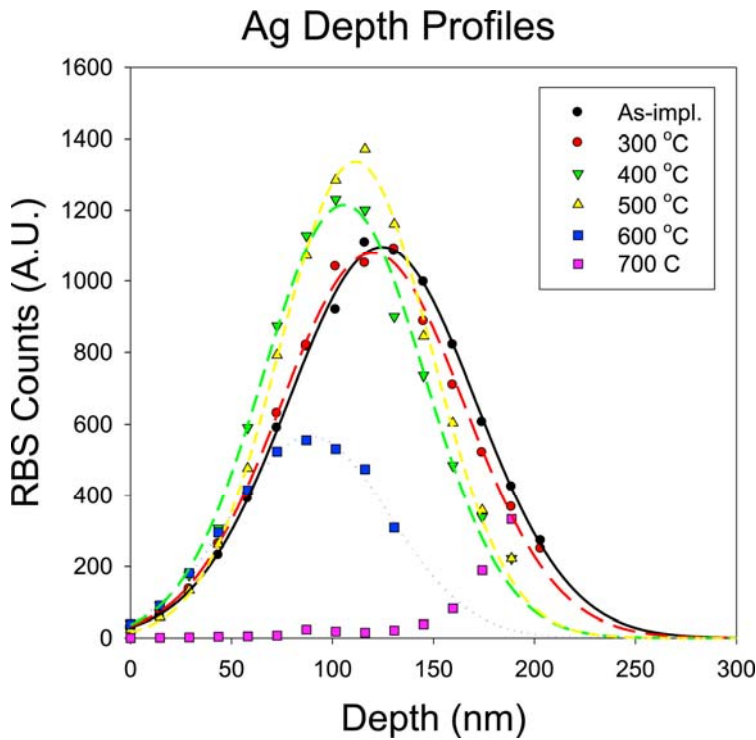


Fig. 8. RBS profiles showing the effect of annealing on the Ag co-implanted distribution in glassy carbon. The dash lines represent Gaussian fits to the experimental data.

Table 5. A comparison of the range parameters obtained from fitting a Gauss function to the experimental Ag profiles after vacuum annealing for 1 h at the temperatures indicated in the table. Also shown is the normalised area under each profile.

Parameter	30 °C	300 °C	400 °C	500 °C	600 °C
Projected Range R_p (nm)	125	120	106	111	89.0
Range Stragglng ΔR_p (nm)	46.4	45.5	40.0	37.6	39.4
Normalised Profile Area	1	0.97	0.95	0.92	0.43

The equation gives the area under a full Gaussian curve.

The normalised area at 600 °C showed that the diffusion of Ag at 600 °C was also accompanied by a loss of Ag, with about 43% of the Ag retained after annealing.

Consequently, the 600 °C RBS data was fitted to the solution of the Fick diffusion equation for an initial Gaussian profile [15] (the 500 °C experimental profile fitted well to a Gaussian equation) to determine a diffusion coefficient for Ag diffusion at 600 °C of about $2 \times 10^{-20} \text{ m}^{-2}\text{s}^{-1}$. The slight broadening made this calculated diffusion coefficient very unreliable, however, as discussed above, the D value obtained is slightly lower to those obtained for the singly implanted Ag glassy carbon samples. The reduction of the rate of diffusion of Ag in the co-implanted glassy carbon samples could be due to the increase in the number of trapping sites (due to the introduction of Sr) which essentially traps the Ag ion in the glassy carbon matrix. Annealing the sample at 700 °C resulted in complete loss of the Ag ions, similarly as for the 360 keV Ag samples.

The RBS profiles of Ag co-implanted with Sr in glassy carbon were compared with those obtained for singly implanted Ag in glassy carbon shown in Fig. 4. A major observation is that the presence of Sr helped with the retainment of Ag in the glassy carbon sample during annealing. At 600 °C, about 23% of the implanted Ag was retained in the singly implanted glassy carbon sample while 43% was retained when the glassy carbon was co-implanted with Ag and Sr.

The effect of annealing on the diffusion of the implanted Sr in the co-implanted glassy carbon sample is shown in Fig. 9. To avoid cluttering of the data which will hinder the reader to see the trends, not all annealed temperatures are shown. Annealing the sample at 300 °C resulted in a slight broadening of the Sr peak with the Sr peak being slightly skewed to the right. This suggests that there was a Fickian type of diffusion of Sr at this temperature. A noticeable feature in the profile is that the implanted Sr did not move deeper into the bulk of the glassy carbon substrate. We have previously investigated the migration behaviour of Sr singly implanted in glassy carbon. One of the key findings in the study is that Sr moved deeper by as much as 40 nm into the glassy carbon substrate at low annealing temperatures [13]. The introduced Ag into the glassy carbon matrix essentially prevents the movement of Sr into the bulk. The SRIM vacancy distributions for both the Sr and Ag implantations predicted a high concentration of the damage introduced in the glassy carbon to be towards the surface with most of the damage introduced by the Ag ions. The non-movement of Sr into the bulk at 300 °C could be due to increased radiation damage (vacancies and interstitials) near the surface of the glassy carbon. This makes the diffusion of Sr towards the surface easier than a further movement into the bulk.

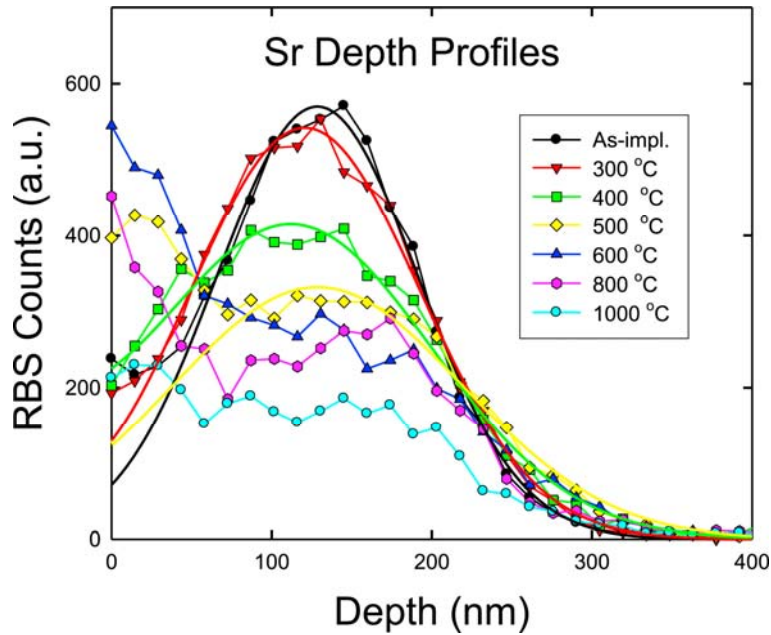


Fig. 9. RBS profile showing the effect of annealing on Sr implanted in glassy carbon. Thicker, smooth solid lines are the fitted solutions to the Fick equation. The thinner, discontinuous lines are drawn to guide the eye as to the trend in the data.

The diffusion co-efficient of Sr in glassy carbon at 300 °C was obtained by fitting the RBS depth profile to the equation given in Ref. [18]. The diffusion co-efficient of Sr in glassy carbon at 300 °C is $1.6 \times 10^{-19} \text{ m}^2/\text{s}$. After annealing at 400 °C, there was further broadening of the Sr peak and a diffusion coefficient of $3.7 \times 10^{-19} \text{ m}^2/\text{s}$ was obtained. After annealing at 500 °C, there was segregation of Sr towards the surface of glassy carbon. However, as can be seen in Fig. 9, a section (i.e. more towards the bulk) of the profile could still be fitted to the equation in Ref. [15]. The results of the fitting did not produce a meaningful diffusion equation as the profile actually became slightly narrower, probably due to the competing segregation. This segregation of the Sr towards the surface was also observed in singly Sr implanted glassy carbon [13]. The driving force for surface segregation is usually minimisation of the Gibbs free energy of the total system. It is expected that this was also the case for the present study. Furthermore, it is not expected to change with increasing annealing temperature, except for the increase mobility of the impurity atoms. As was discussed for the damage profile (dpa) of Fig. 1, the microstructure does not change significantly with annealing temperature. Annealing at 600 °C to – 1000 °C resulted in further segregation of Sr towards the surface of glassy carbon and a complete disappearance of an approximate Gaussian profile which were still partially visible in the 500 °C profile. The segregation of Sr was accompanied by a loss of Sr from the glassy carbon – see Fig. 10. The amount of retained Sr ions after each annealing is presented in Fig. 8. The amount of retained Sr ions was estimated by adding the number of Sr counts present in each profile and comparing it with the as-implanted profile. This method was the preferred choice because the Sr peaks (especially at high annealing temperatures) could not be fitted with a Gaussian profile to obtain the normalised yield. A comparison between the data points and the fitted curve for the as-implanted (see Fig. 9) shows that there was an Ag contribution near the surface due to overlapping of the Ag and Sr RBS profiles. This overlap makes it impossible to fit the RBS profiles especially at high annealing temperatures. Fig. 9

shows that there was already significant loss of Sr at 500 °C. The loss of Sr is significant at higher temperatures. Only about 43% of the implanted Sr was retained after annealing the

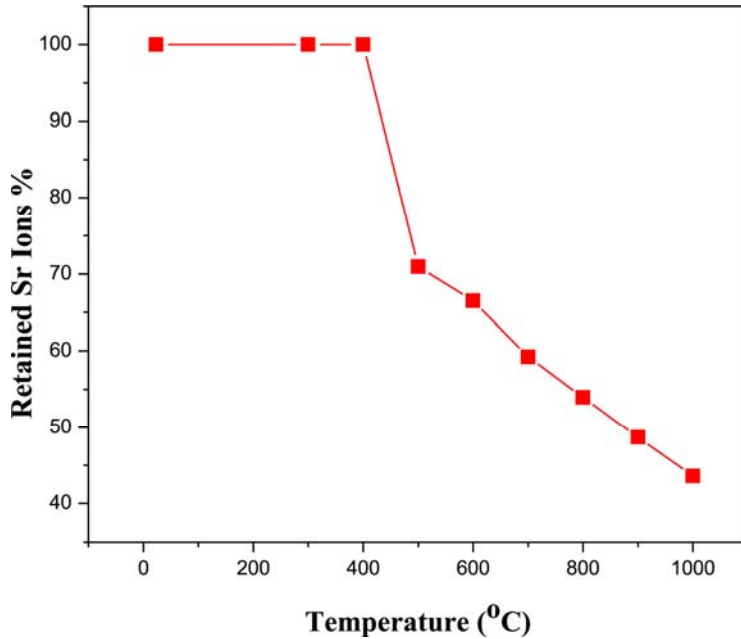


Fig. 10. Graph showing the amount of retained Sr ions after annealing.

3. Conclusion

The diffusion behaviour of Ag, Sr and Ag co-implanted in glassy carbon has been investigated by using Rutherford backscattering spectrometry (RBS). For the glassy carbon sample singly implanted with Ag, there was no noticeable Fickian diffusion at 300 °C and 400 °C. However, at 500 °C, limited Fickian diffusion of Ag was observed. The diffusion of Ag at this temperature was accompanied by loss of Ag. Distinct Fickian diffusion of Ag in glassy carbon was observed at temperatures ranging from 500 °C, 550 °C and 575 °C respectively and the diffusion coefficients at these temperatures were obtained. At elevated annealing temperature, there was significant loss of Ag from the surface of the glassy carbon.

For the Sr and Ag co-implanted glassy carbon samples, the diffusion behaviour of Ag co-implanted with Sr is very similar to that of the Ag singly implanted in glassy carbon samples. However, the introduction of Sr assisted in the retainment of Ag after annealing. At 500 °C, only about 78% of the implanted Ag was retained in the singly implanted glassy carbon samples while 92% of the implanted Ag was retained in the co-implanted glassy carbon sample.

The introduction of Ag into the matrix changed the diffusion behaviour of Sr at low annealing temperatures. At 300 °C, there was no movement of the implanted Sr deeper into the bulk of the glassy carbon substrate. This non-diffusion into the bulk was attributed to the increase in the damage created in the near surface region of the glassy carbon due to the co-implantation of both the Sr and Ag ions. The diffusion coefficient of Sr in glassy carbon at 300 °C was estimated as $D = 1.6 \times 10^{-19} \text{ m}^2/\text{s}$ and at 400 °C as $D = 3.7 \times 10^{-19} \text{ m}^2/\text{s}$.

The diffusion of Sr at 500 °C was accompanied by the segregation of the implanted Sr towards the surface of the glassy carbon. At higher annealing temperatures the diffusional behaviour of the implanted Sr was completely dominated by the segregation effects. The segregation of Sr was elevated and accompanied by loss of Sr at the higher annealing temperatures.

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