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Surface and interface modification of Zr/SiC interface by swift heavy ion irradiation

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ABSTRACT

In this study thin Zr films (135 nm) were deposited on 6H-SiC substrate at room temperature by sputter deposition. The Zr/SiC couples were irradiated by 167 MeV Xe²⁶⁺ ions at room temperature at fluences of 5.0×10^{12} , 1.0×10^{13} , 5.0×10^{13} , 2.0×10^{14} , 3.1×10^{14} and 6.3×10^{14} ions/cm². The samples were analysed before and after irradiation using Rutherford backscattering spectroscopy (RBS), atomic force microscopy (AFM) and secondary electron microscopy (SEM). The surface morphology from SEM analysis revealed a homogeneous Zr surface which did not vary with increasing fluences of irradiation. AFM analysis revealed that the R_{rms} surface roughness did increase from the as-deposited value of 1.6 nm and then decrease at higher SHI irradiation fluences to 1.4 nm. RBS results indicate that interface mixing between Zr and SiC interface occurred and varied linearly with irradiation ion fluence. The value obtained for diffusivity of Zr shows that the mixing was due to interdiffusion across the interface during a transient melt phase according to the thermal spike model.

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1. Introduction

Silicon carbide (SiC) has various applications in different technological fields as a structural material and a semiconductor. It acts as the main diffusion barrier of fission products in coated particle nuclear fuels such as the pebble bed modular reactor (PBMR). SiC has been considered for use as a reinforcement material in metal–ceramic composites for high temperature nuclear applications [1]. These composites rely on SiC high-temperature properties, chemical stability, low density and reduced neutron activation [2]. Zirconium is used as the metal in metal–ceramic composites and also in metal matrix microencapsulated (M3) fuel. This new form of nuclear fuel structure was proposed by Terrani et al. [3]. M3 fuel consists of TRISO or bi-structural isotropic (BISO) fuel particles embedded in a Zr metal matrix to form an integral fuel rod.

The strength of metal–ceramic composite materials is determined by the nature of physical and chemical bonding characteristics. Stable interfaces between metal and SiC are necessary for the structural integrity of these composites. Metal–ceramic composite materials such as Zr–SiC, offer the potential to be the next generation of materials for high temperature applications [4].

These composites have also been proposed as a possible fuel structure for high temperature reactors (HTR) with the aim of reducing the metal fraction in the composite, while maintaining a low neutron absorption cross-section close to the Zr one. Porta et al. proposed a fuel design with PuO₂ particles coated by a layer of SiC embedded in a mixed SiC/Zr matrix [5]. The ratio of SiC to Zr in the proposed metal–ceramic matrix was 55–35, respectively. These ceramic–metal matrices have a high SiC content, therefore increasing the surface area available for Zr/SiC interactions.

In the above mentioned applications, the Zr/SiC contacts are subjected to irradiation by fission fragments which may lead to atomic mixing at the Zr/SiC interface. The interactions which can occur in Zr/SiC materials may lead to interface modification known as ion beam mixing. This can occur at the interfaces of these metal/ceramic composites leading to the degradation of these structural materials. The stability and degradation of these contacts needs to be investigated. It is important to understand the basic mechanisms of phase transformations between Zr and SiC under irradiation with heavy ions, at energies (MeV range) in the electronic stopping power regime, corresponding to the energy of fission fragments.

Irradiation with ions in keV and MeV energy regimes can induce atomic migration across an interface in metal/ceramic systems. Such experiments can therefore investigate the radiation stability of such materials. The incident ions lose energy as they traverse

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through the material which is either spent in displacing atoms (of the sample) by elastic collisions or in exciting (or ionizing) the atoms by inelastic collision. This energy loss can be categorised into nuclear (S_n) and electronic stopping (S_e) which are dominant at low and high energies, respectively.

Swift heavy ion (SHI) irradiation (>1 MeV) can simulate the irradiation (electronic stopping) when energetic particles interact with the samples during the slowing down of particles while traversing the materials. The effect of SHI irradiation on a material is known to depend on ion energy, fluence and ion species [6]. These effects include intermixing at interfaces, modification of surface and interface roughness, defect annihilation or creation, and latent track formation [6].

Two models exist which qualitatively explain the interface intermixing induced by energy transfer from SHI irradiation, these are the thermal spike [7] and the Coulomb explosion models [8]. According to the thermal spike model, incident ions lose energy predominantly by electronic excitation and ionization of the target atoms. The excited electrons transfer energy to phonons via electron–phonon coupling resulting in a thermal spike (>1000 K) developing transiently along the ion path in the lattice subsystem [9]. This transient temperature spike lasts for about 10^{-12} s [7] and can cause two layers at an interface to attain a molten state, leading to intermixing of atomic species involved.

Although metals are generally less sensitive to SHI irradiation, Wang et al. [7] suggested that transition metals such as Bi, Fe, Zr and Ti are sensitive. Wang et al. state that Zr is sensitive to electronic excitation beyond a certain electronic energy loss (S_e) of approximately 30 keV/nm [7]. Previous work on Zr/Si SHI irradiation studies has been performed by Sisodia et al. [10] and Agarwal et al. [11] using Au ions at 350 and 120 MeV, respectively and they observed intermixing to occur. The width of the mixing zone was observed to increase in magnitude with the irradiating ion fluence. The ZrSi phase was the only silicide observed to form at the intermixed region between Zr and Si. Nagel et al. [12] studied the irradiation effects on Cu, Ni and Pt thin films deposited on SiC substrates. Their samples were irradiated with 150 keV Ar⁺ ions. This energy falls under the nuclear energy loss regime and they did observe intermixing and phase formation to occur at the metal/SiC interfaces [12].

In this study, we investigate the effect of 167 MeV Xe ions SHI irradiation at room temperature on Zr/SiC. Interface mixing between Zr and SiC would indicate interface mixing due to large electronic excitations. The mixing will be quantified by calculating mixing rate and diffusivity. The Zr thin film surface modification by SHI irradiation will also be investigated. A survey of the available literature reveals no experimental investigations on SHI irradiation of Zr/SiC.

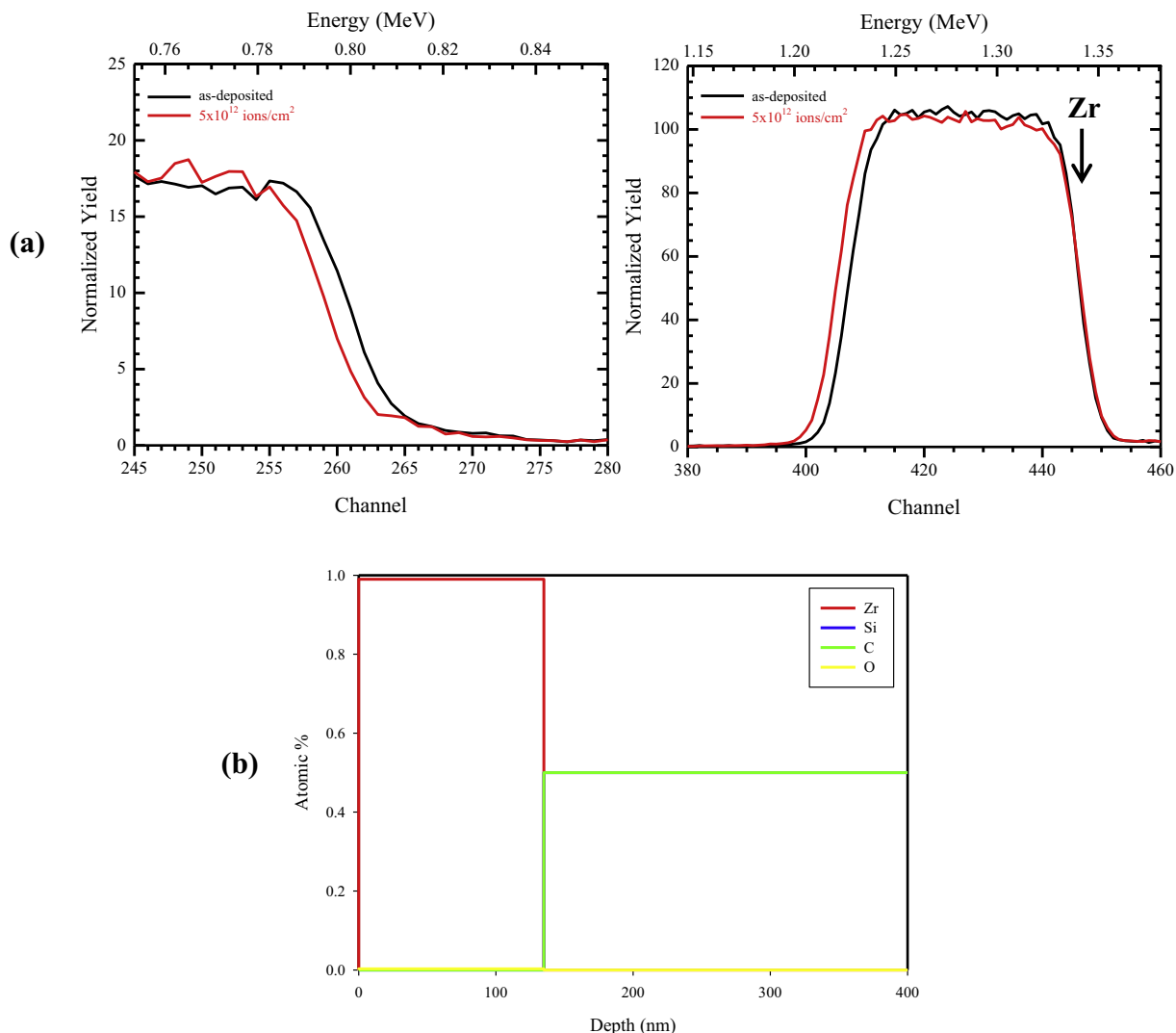


Fig. 1. (a) Overlay of RBS spectra of as-deposited and sample irradiated at fluence of 5.0×10^{12} ions/cm² (b) depth profile of as-deposited sample.

2. Experimental method

Zr thin films were deposited on 6H-SiC single-crystal wafers using Orion 5 sputtering system (AJA international Inc.). The chamber was pumped down to a base pressure of 10^{-7} Torr and then backfilled with Ar gas to a pressure of 10^{-3} Torr. The Zr target and the SiC substrate were sputter-cleaned for 10 min using Ar plasma before the room temperature deposition was performed. This ensured the removal of the native oxide layer from the SiC wafer and a clean Zr target surface for sputtering since Zr readily oxidizes in air. The samples were uniformly irradiated at room temperature by 167 MeV Xe^{26+} ions at the joint institute of nuclear research (JINR), Dubna. The ion fluences were set at 5.0×10^{12} , 1.0×10^{13} , 5.0×10^{13} , 2.0×10^{14} , 3.1×10^{14} and 6.3×10^{14} ions/cm².

All the samples were analysed by Rutherford backscattering spectrometry (RBS) before and after irradiation. The energy of the He^+ ions was 1.6 MeV with a scattering angle of 165° . RBS analysis was performed to obtain the elemental composition of the as-deposited and irradiated samples, the thickness of deposited Zr

film and the thickness of the mixed zone. The surface morphology of the Zr thin film deposited on 6H-SiC was studied by scanning electron microscope (SEM) and atomic force microscopy (AFM) before and after SHI irradiation. The Zeiss Ultra 55 field emission scanning electron microscope was used for surface morphology analysis of the Zr thin film deposited on 6H-SiC samples. The SEM analysis of the surface of the Zr film was performed by the Zeiss Ultra 55 field emission scanning electron. This was done at low beam energy of 2 kV to reveal surface features before and after irradiation. The AFM images were obtained using the Dimension Icon AFM system, working in contact mode in an air ambient. The AFM images were obtained and analysed using NanoScope Analysis (Bruker, USA) software. In this study, the AFM images analysed were of $2 \times 2 \mu\text{m}$ scan sizes for the as-deposited and irradiated samples.

3. Results and discussion

The quantitative RBS analysis was performed by fitting the RBS spectra with the RUMP computer code [13]. The ion range and

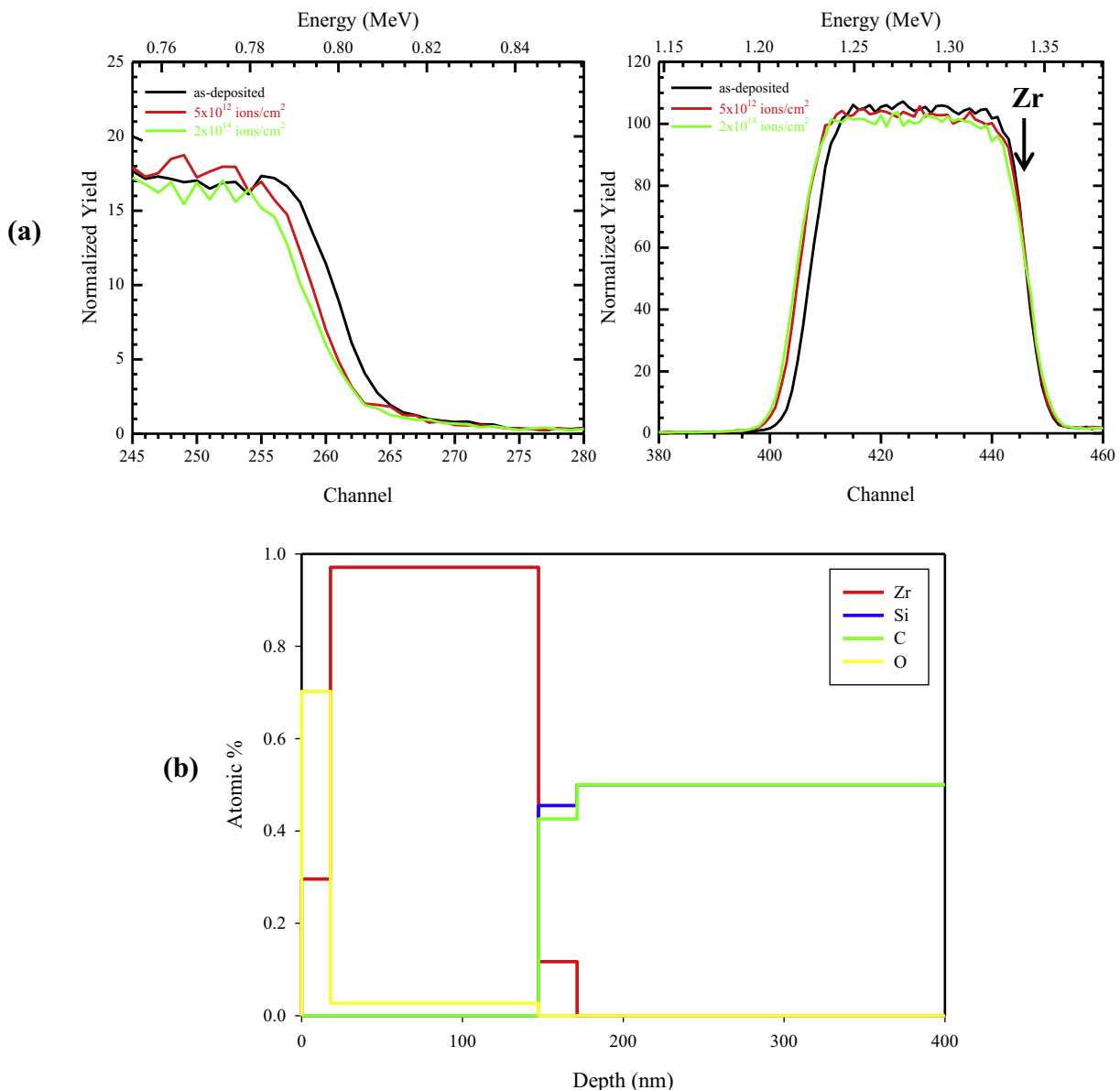


Fig. 2. (a) Overlay of RBS spectra of as-deposited, samples irradiated at fluence of 5.0×10^{12} and 2.0×10^{14} ions/cm² (b) depth profile of sample irradiated at fluence of 2.0×10^{14} ions/cm².

energy loss values were calculated by the Monte Carlo computer programme SRIM-2013 [14]. The electronic energy loss of 167 MeV Xe in Zr and SiC were found to be 23.75 keV/nm and 20.42 keV/nm, respectively, while the nuclear energy loss values were 0.122 keV/nm and 0.084 keV/nm for Zr and SiC, respectively. This indicated that energy loss of incident Xe ions was via electronic excitation from inelastic collisions and not nuclear elastic collisions.

The ion-induced changes at the Zr/SiC interface were deduced by careful RBS measurements and the thickness of mixing zone was measured from RUMP simulations. Fig. 1(a) illustrates the RBS spectra of Zr/SiC samples before and after irradiation at a fluence of 5.0×10^{12} ions/cm². The arrows indicate the surface

position of Zr, while the black and red line spectra denote the as-deposited and irradiated samples, respectively. The RUMP simulations of the RBS spectra fit very well to the spectra of the as-deposited and irradiated samples. The RBS spectrum of the as-deposited sample indicates that the Zr/SiC interface was sharp and this can be deduced from the low energy edge of the Zr peak which falls off sharply. The thickness of the deposited Zr layer was calculated from RUMP simulations and found to be 135 nm which can be considered as thin film.

After irradiating with Xe ions at a fluence of 5.0×10^{12} ions/cm², slight interdiffusion was observed to occur as seen in Fig. 1(a). A reduction in the Zr peak was observed accompanied by the widening of this peak. The slope of low energy edge and

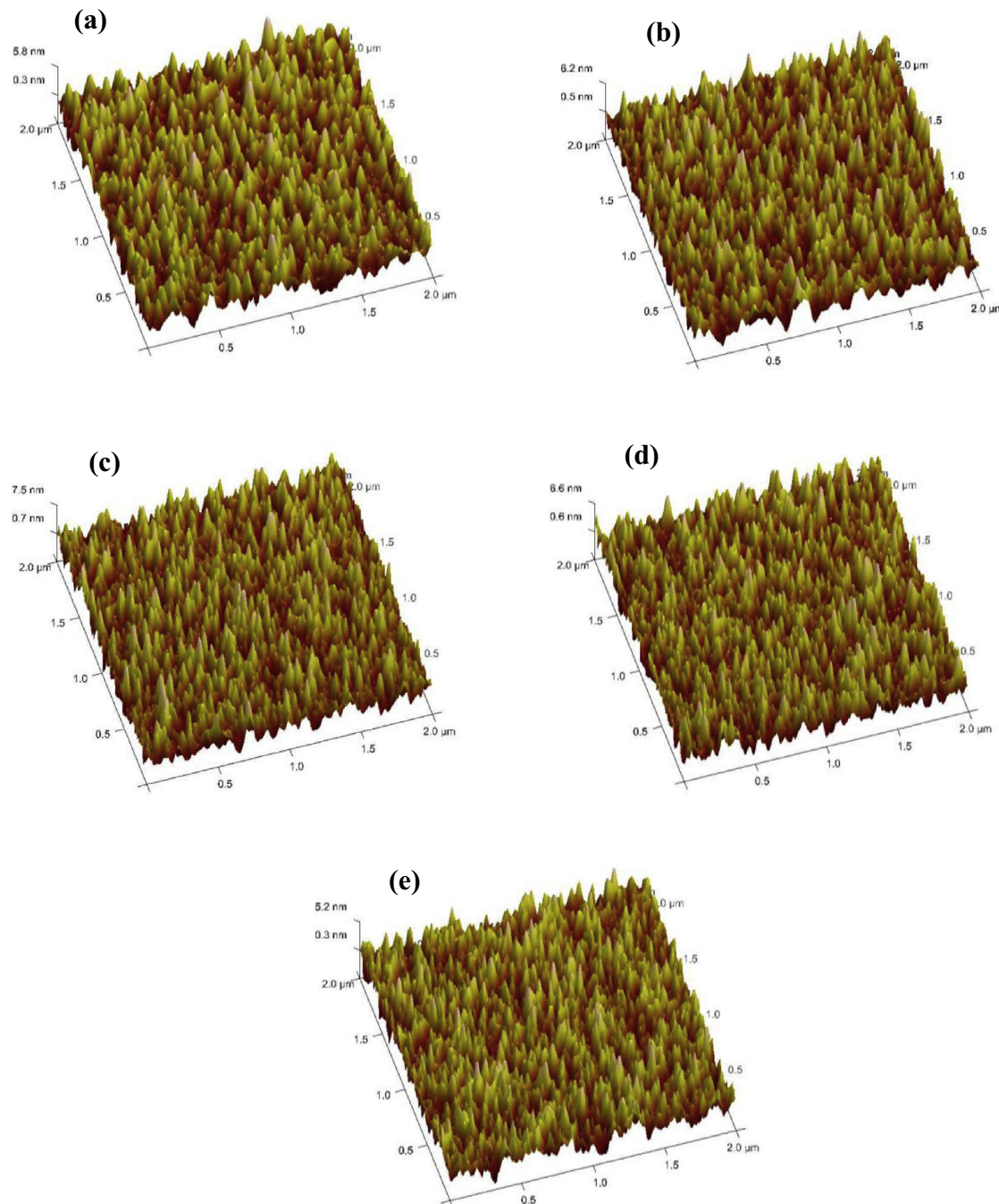


Fig. 3. AFM images of (a) as-deposited and irradiated samples at (b) 5.0×10^{12} , (c) 1.0×10^{13} , (d) 5.0×10^{13} and (e) 2.0×10^{14} ions/cm².

high energy edge of the Zr and Si peaks respectively were observed to change. The Zr low energy edge was observed to shift towards the Si edge while the Si high energy edge shifted towards the bulk of SiC. A thin intermixing zone was initially observed to form at this fluence of irradiation.

The RBS spectra of sample irradiated at a fluence of 1.0×10^{14} ions/cm² was found to be similar those irradiated at 5.0×10^{13} ions/cm² and the two spectra overlaid each other. Zr was observed to further diffuse into SiC and the Si edge shifted further to lower channels after irradiating at fluence of 5.0×10^{13} ions/cm². After irradiating at a fluence of 2.0×10^{14} ions/cm², further shift of Zr peak into the bulk can be observed as seen in Fig. 2(a). A small step at the bottom of Si high energy edge can be observed to form. The Si and C concentrations varied slightly with increase in irradiation fluence but remained near stoichiometric composition of SiC with a slight increase in Zr concentration.

These results suggest that interface mixing between Zr and SiC did occur due to SHI irradiation. The width of the intermixed region was also observed to increase with the magnitude of ion fluence. The RUMP simulations of RBS data indicate that Zr diffused into SiC due to SHI irradiation leading to the formation of an intermixed zone of about 28 nm wide at fluence of 3.1×10^{14} ions/cm². No further interdiffusion was observed to occur after irradiating with fluences greater than 3.1×10^{14} ions/cm². It should be stated that the Zr surface did get oxidised after irradiation with the formation of a very thin ZrO₂ layer. This was observed to grow slightly wider with increase in the irradiation ion fluence.

The mixing at the Zr/SiC interface is a result of displacement of Zr atoms by electronic excitation, which can be explained by the thermal spike model. The mixing could not be due to Coulomb explosion since it is predominant in insulators but in metals or semiconductors the ionized atoms are usually quickly neutralised. The ratio of S_e to S_n of Zr and SiC is 194 and 243 respectively indicating that the effect of elastic collision is negligible.

The effect SHI irradiation on the surface structure of the Zr thin films was measured by SEM and AFM analysis techniques. The analysis of the SEM micrographs did not show any visible change on the Zr surface and these are not presented here. AFM images of unirradiated and irradiated Zr/SiC samples are shown in Fig. 3. The root mean square roughness (R_{rms}) of the Zr surface was calculated from the AFM images. The R_{rms} roughness of the as-deposited Zr surface was low at a value of 1.6 nm. This was observed to remain constant after irradiating at fluence of 5×10^{12} ions/cm² and then increase after 1×10^{13} and 5×10^{13} ions/cm² irradiations to a maximum value of 1.89 nm. Further irradiation led to decrease of R_{rms} value to 1.4 nm at high ion fluences of 2×10^{14} ions/cm². The AFM images of the as-deposited and irradiated sample at fluences of 5×10^{12} ions/cm² are similar and show small granular structure on the surface of the Zr thin film. AFM analysis indicated that the lateral size of the surface features decreased with increase in the fluence of ion irradiation. This led to the appearance of narrower structures on the Zr surface as seen in Fig. 3(c–d). The reduction in granule size could be due to the sputtering of surface structures as a result of multiple ion impacts on the surface and smoothening induced by material transport during surface diffusion at higher irradiation fluence [15].

The Zr/SiC interface variation as a function of ion fluence was calculated from data obtained from RBS measurements. This enabled us to calculate the mixing rate and the diffusion coefficient for Zr. The diffusion coefficient is expressed as:

$$D = \frac{\Delta\sigma^2}{2t_n} \quad (1)$$

where $\Delta\sigma^2$ is the spatial width of Zr at the interface due to irradiation, t_n is the diffusion time given by:

Table 1
Zr/SiC interface width, variance and mixing rate with fluence.

Fluence Φ (ions/cm ²)	Interface width σ (nm)	Interface variance $\Delta\sigma^2$ (nm) ²	Mixing rate $k = \Delta\sigma^2/\Phi$ (nm ⁴ /ion)
as-deposited	–	–	
5.0×10^{12}	18	324	
5.0×10^{13}	21	441	108
2.0×10^{14}	25	576	
3.1×10^{14}	28	676	

$$t_n = \left(\frac{\Phi}{\Phi_c} \right) t_s \quad (2)$$

where Φ is the maximum fluence, $\Phi_c = 1/(2r)^2$ is the fluence for complete overlap of the ion tracks, t_s is the duration of melt phase of Zr. The values of r and t_s for Zr are not available and were approximated to 1.5 nm and 1 ps respectively from Ni as has been done by other authors in the case with transition metals such as Zr, Co and V [7,11,16,17].

From RUMP simulation of the RBS spectra of samples irradiated at different fluences, the values of interdiffusion width σ , interface variance $\Delta\sigma^2(\Phi)$ and the mixing rate k were calculated and are tabulated in Table 1. A plot of interface variance versus ion fluence is illustrated in Fig. 4 and it can be observed that the interface variance increased linearly with the increase in ion fluence. The slope of linear fit of this graph gives the mixing rate k which was found to be 108 nm⁴/ion.

The mixing rate value obtained is small since SiC is not sensitive to electronic excitation while Zr is. SiC has a very high resistance to SHI irradiation with threshold of electronic stopping power for track formation >34 keV/nm which only leads to the production of point defects [18]. The high resistance of SiC to SHI irradiation was postulated by Zinkle et al. [19] to be due to the high thermal conductivity of SiC. The interface diffusivity D was calculated using Eq. (1) and was found to be 5.5×10^{-6} m² s⁻¹. This value is in the same magnitude with diffusivity found in liquid metals and therefore implies that interface mixing occurred in the melt phase [20]. This suggests that interface mixing occurred according thermal spike model and excludes solid-state diffusion.

In this study Zr has an electronic energy loss of 23.75 keV/nm which is slightly lower than the reported threshold electronic energy loss value of 30.0 keV/nm [7], but mixing was observed to occur. Agarwal et al. [11] observed intermixing to occur between Zr and Si at electronic energy loss value of 24.36 keV/nm which

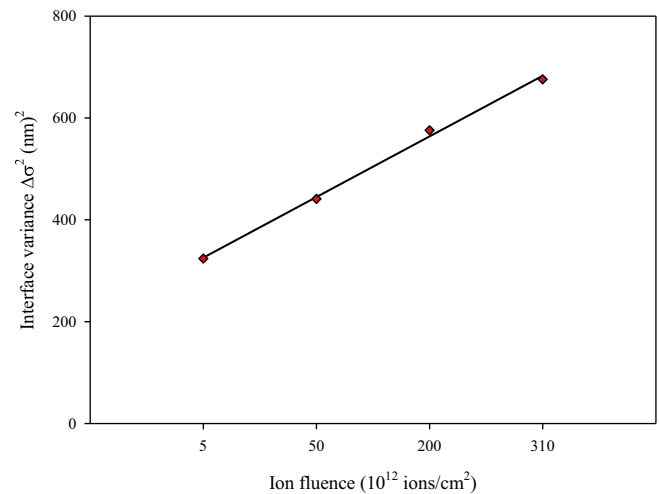


Fig. 4. Variation of interface variance $\Delta\sigma^2$ with the ion fluence.

is also below the electronic energy loss threshold value. It has been reported that in thin films, SHI irradiation can induce interface mixing at substantially lower values of electronic energy loss compared to bulk materials [6] as was observed in this study.

4. Conclusion

This study demonstrates the interface mixing between Zr and SiC was induced by SHI irradiation by 167 MeV Xe ions at fluences of 5.0×10^{12} to 6.3×10^{14} ions/cm² as indicated by the RBS analysis technique. The width mixing region in the Zr/SiC interface varies almost linearly with the magnitude of irradiation ion fluence. The value obtained for diffusivity suggested that the mixing is due to interdiffusion across the interface during a transient melt phase following the thermal spike model. Zr surface roughness and granule size was observed to vary due to SHI irradiation fluence.

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