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Interface reactions between Pd thin films and SiC by thermal annealing and SHI irradiation

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ABSTRACT

The solid-state reactions between Pd thin films and 6H-SiC substrates induced by thermal annealing, room temperature swift heavy ion (SHI) irradiation and high temperature SHI irradiation have been investigated by in situ and real-time Rutherford backscattering spectrometry (RBS) and Grazing incidence X-ray diffraction (GIXRD). At room temperature, no silicides were detected to have formed in the Pd/SiC samples. Two reaction growth zones were observed in the samples annealed in situ and analysed by real time RBS. The initial reaction growth region led to formation of Pd_3Si or (Pd_2Si + Pd_4Si) as the initial phase (s) to form at a temperature of about 450 °C. Thereafter, the reaction zone did not change until a temperature of 640 °C was attained where Pd_2Si was observed to form in the reaction zone. Kinetic analysis of the initial reaction indicates very fast reaction rates of about 1.55×10^{15} at cm^{-2}/s and the Pd silicide formed grew linear with time. SHI irradiation of the Pd/SiC samples was performed by 167 MeV Xe^{26+} ions at room temperature at high fluences of 1.07×10^{14} and 4×10^{14} ions/cm^2 and at 400 °C at lower fluences of 5×10^{13} ions/cm^2. The Pd/SiC interface was analysed by RBS and no SHI induced diffusion was observed for room temperature irradiations. The sample irradiated at 400 °C, SHI induced diffusion was observed to occur accompanied with the formation of Pd_4Si, Pd_9Si_2 and Pd_5Si phases which were identified by GIXRD analysis.

1. Introduction

Silicon carbide (SiC) is a ceramic and semiconductor material that has various applications in different technological fields as a structural material and in electronics. In coated particle nuclear fuels such as the tristructural-isotropic (TRISO) fuel particles, used in the pebble bed modular reactor (PBMR), SiC is the main diffusion barrier of fission products (FPs) and also provides structural integrity to the fuel particle. These applications rely on SiC high-temperature properties such as chemical stability, low density, wide band gap, small neutron capture cross-section and stability under neutron irradiation [1]. Pd is one of the FPs that can react with SiC under high temperature and radioactive environment leading to thinning of the SiC layer. This may lead to reduction in the strength of this layer and result in the release of radioactive FPs such as Cs, Ag and Sr [2].

Very sensitive high temperature hydrogen and hydrocarbon gas detectors can be fabricated from Pd/SiC Schottky diodes [3,4]. These sensors are necessary for many technological applications such as nuclear reactors where it is essential to monitor hydrogen levels for reactor safety. Hydrogen is usually formed in radioactive waste tanks, during plutonium reprocessing, through the radiolysis of water or via the unwanted reaction of water with high temperature reactor core and cladding materials (uranium oxide, zirconium) [5].

In this environment the Pd/SiC contacts would be exposed to high temperatures and irradiation by fission fragments which may lead to interactions or atomic mixing at the Pd/SiC interface. These interactions may lead to the degradation of the SiC layer and Pd/SiC contacts. It is important to understand the basic mechanisms of phase transformations between Pd and SiC under irradiation with heavy ions, at energies (MeV range) in the electronic

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stopping power regime, corresponding to the energy of fission fragments.

Swift heavy ion (SHI) irradiation can simulate the irradiation (electronic stopping) when energetic particles interact with the samples during the slowing down of particles while traversing the materials. The effects of SHI irradiation on a material include intermixing at interfaces, modification of surface and interface roughness, defect annihilation or creation, and latent track formation [6]. The energy from SHIs can be transferred to the target atoms which are then pushed from their lattice positions and collide with other atoms creating a recoil cascade. This recoil cascade may move beyond the interface of a layered system and may result in atomic mixing in the vicinity of interface [7]. In this way SHI irradiation can also be applied in modification of material electrical, optical and structural properties.

Since, interface structure and silicide formation at Pd/SiC interfaces is of vital interest in TRISO and hydrogen sensor device applications, there is need to understand the properties of these metal–semiconductor interfaces. Electronic changes in Pd/SiC Schottky diodes have been observed after annealing and these can be explained by investigating the surface and interface changes in the Pd/SiC contacts. Understanding the kinetics and reaction mechanisms of the Pd/SiC system under temperature and irradiation effects is critical in extending the lifetime of TRISO fuels and hydrogen gas sensors as this would address long-term high temperature operation of Pd/SiC Schottky diode.

In this work, our interest is the detection of the onset of the formation of phases, identify the phases formed, phase evolution and determine the growth kinetics from a single sample in one experimental run. In situ and real-time RBS which involves obtaining the RBS spectrum while annealing of a sample, provides the atomic depth profile continuously as a function of temperature and time was applied to achieve this [8]. We also investigate the effect of 167 MeV Xe^{26+} ions SHI irradiation at room temperature and at 400 °C on the Pd/SiC interface. Interface mixing between Pd and SiC would indicate interface mixing due to large electronic excitations. The phases formed will be identified and the sample interface modification by thermal annealing, room temperature and high temperature SHI irradiation will also be investigated. To the best of our knowledge, no experimental investigations on SHI irradiation of Pd/SiC contacts have been reported.

2. Experimental method

The 6H-SiC single-crystal, semi-insulating wafers (Pam-Xiamen, China) were cut into 5×5 mm^2 pieces by a diamond scriber and thereafter cleaned by chemical treatment to remove any contamination and the native oxide layer. The Pd thin films were deposited by resistive evaporation technique at base pressure of 1.0×10^{-7} mbar and 9.0×10^{-6} mbar during evaporation. The Pd film thickness was monitored by a calibrated Inficon deposition rate monitor. The rate of deposition was kept between 0.2 and 0.4 Å/s until the required thickness of 140 nm was obtained.

Real-time Rutherford backscattering spectrometry (RBS) analysis of the Pd/SiC samples was performed in situ (iThemba Labs) in a chamber with a copper heating stage allowing the samples to be annealed and analysed simultaneously. The RBS spectra were obtained typically with 1.6 MeV He^+ particles at a backscattering angle of 165° with the sample was tilted 10° away from the normal. Real-time RBS analysis was carried out at pressures of around 10^{-7} mbar and the beam current was in the range 40–50 nA. Annealing was performed either isothermally or with a linearly ramped temperature profile as illustrated in Fig. 1(a) while acquiring RBS spectra at periodic time intervals.

Other set of Pd/SiC samples were uniformly irradiated at room temperature by 167 MeV Xe^{26+} ions at the Joint Institute for Nuclear Research (JINR), Dubna. The ion fluences were set at 1.07×10^{14} and 4×10^{14} ions/cm^2 for room temperature irradiation and at 5.0×10^{13} ions/cm^2 for irradiation at 400 °C. The SHI irradiated samples were analysed at the University of Pretoria RBS facility by a van der Graaff accelerator with 1.6 MeV He^+ ions at a backscattering angle of 165° and the sample was tilted 4° away from the normal. The beam current was maintained at 15 nA. X-ray diffraction (XRD) analysis of all the Pd/SiC samples was performed by a Bruker-AXS D8 Advance diffractometer in the glancing incidence geometry using a Cu K_α radiation source. Grazing incidence XRD (GIXRD) geometry in the 2θ range of 30–70° was used to prevent the X-ray radiation from penetrating into the SiC substrate.

3. Results and discussion

In this study, individual RBS spectra were analysed using the RUMP code and semi-automatic PERT subroutine [9]. This was done to obtain the thickness of the thin films, composition of the reaction zone, to ascertain the temperature of initial reaction, monitor interdiffusion across the interface and chemical reactions between Pd and the SiC substrate. The quantitative RBS analysis was performed by simulating the RBS spectra of as-deposited, in situ annealed and SHI irradiated samples. An overlay of the simulated and raw RBS spectra of the as-deposited sample is shown in Fig. 1(b). From the simulation of the as-deposited RBS spectrum approximately 140 nm of Pd thin film deposited on SiC substrate was obtained. The sharp edges of the Pd signal indicate a Pd thin film layer with a sharp interface with the SiC substrate.

The initial in situ annealing was performed by ramping the temperature at a fast rate of 20 °C min^{-1}, from room temperature to 160 °C and thereafter at a slower linear ramp rate of 2 °C min^{-1} up to 600 °C. This was performed to identify the temperature at which reactions between Pd and SiC occurred. No reaction or interdiffusion was observed after annealing up to at a temperature of 426 °C. It was observed that the RBS spectrum of the sample annealed at 426 °C is not significantly different from the as-deposited one as seen in Fig. 1(b). From a temperature of 450 °C (150 min annealing) interface diffusion began to take place as observed by the changes in the slope of Pd back edge and of the Si high energy edge. For the second sample, the temperature was initially ramped at a rate of 20 °C min^{-1} up to 450 °C and held constant for 90 min. The temperature was thereafter increased at a ramp rate of 2 °C min^{-1} to 650 °C and held there for 80 min to ensure complete reaction of the Pd thin film as illustrated in Fig. 1(a).

Fig. 1(c) illustrates the RBS spectra obtained in real time. The RBS spectra have been stacked along the time axis to form a three dimensional plot. This gives the complete picture of interface reactions occurring in a single sample during the annealing process. Since some features are sometimes hidden behind others, it is convenient to plot the data using contour lines as shown in Fig. 1(d). The contour plot consists of a number of a single RBS spectra obtained after every 2 min at certain temperature resulting in a composite of 150 RBS spectra plotted against the backscattering energy. The 3D RBS spectra and the contour plot indicate that no observable intermixing at the interface between Pd and SiC before 43 min (450 °C) could be detected. In Fig. 1(c) and (d) two distinct growth regimes can be observed for the reaction between Pd and SiC. The area between the dashed lines in Fig. 1(d) indicates the regions where the different stages of interface reaction occurred. The onset of reactions between the Pd thin film and SiC substrate is clearly visible after 43 min which is about 20 min after reaching

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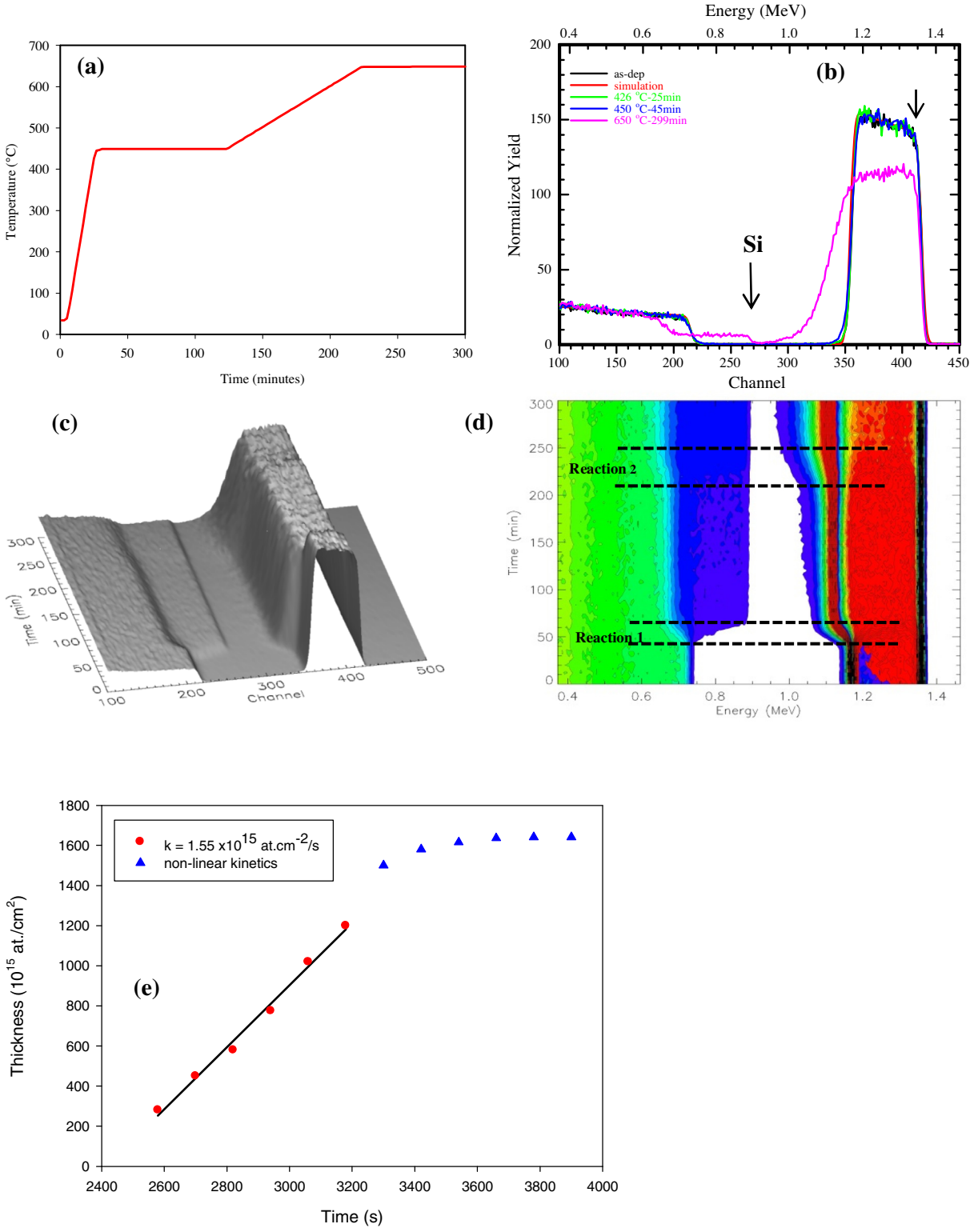

Fig. 1. (a) Different temperature ramp anneal used for in situ annealing (b) overlay of RBS spectra and simulation of as-deposited and annealed samples (c) three dimensional plot of RBS spectra (d) contour lines of RBS spectra obtained during in situ RBS analysis (e) Plot of reaction zone thickness versus time during Reaction 1 at 450 °C.

450 °C. This delay in the onset of the reaction must be associated with an incubation period that is not yet understood. Previous work [10] suggests that carbon produced from dissociation of SiC at the Pd/SiC interface first diffuses into the overlaying Pd layer before any silicide phases were detected.

The contour illustration in Fig. 1(d) shows that the solid state reactions start at a temperature of about 450 °C. The reactions between Pd thin film and SiC were very fast and the growth rate was high in this region, therefore there were few data points available for analysis since the RBS spectra were acquired every 2 min.

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Height of the step on Si high energy edge step remained the same after annealing above 450 °C but step grew wider. This indicated that the same phase(s) were present but the thickness of the reaction zone (RZ) increased with annealing temperature and duration. The RUMP simulations indicate a Pd:Si atomic ratio close to 3:1 suggesting the formation of Pd_3Si or ($Pd_2Si + Pd_4Si$). The reaction rate for this region starts to decelerate after 65 min of annealing. A plot of the reaction zone thickness versus annealing time from values obtained from RUMP simulations is presented in Fig. 1(e). Two distinct growth regimes, linear and non-linear can be observed from this graph and the linear growth represents reaction 1 indicated in Fig. 1(d). The linear region is characterised by very fast reaction rate ($k = 1.55 \times 10^{15}$ at cm^{-2}/s) which slows down after annealing for 65 min. The reaction rate was calculated by obtaining the slope of the linear region using the expression $x = kt$, where x is the thickness of the reaction zone, t is the annealing duration, and k is the reaction rate constant.

The second reaction regime was observed to occur after annealing for 210 min and at a temperature of 640 °C (see Fig. 1(a)). This RZ growth was characterised by a further shift of the Pd back edge towards lower energy channels and top the Si edge towards low energy channels as see in Fig. 1(c) and (d). It was observed that the RZ had extended through the entire 140 nm Pd thin film after 250 min annealing duration at a temperature of about 650 °C; after which no further change in the RBS spectra was observed. The reactions in this region proceeded at a much slower rate by the consumption of the initial Pd silicides phase(s) by thermal decomposition process to form Pd_2Si. This is the first time that such reaction mechanism between Pd and SiC has been reported where two different reaction regimes exist.

For the SHI irradiation experiments, the ion range and energy loss values were calculated by the Monte Carlo computer programme SRIM-2013 [11]. The electronic energy loss of 167 MeV Xe in Pd and SiC were found to be 40.68 keV/nm and 20.42 keV/nm respectively, while the nuclear energy loss values were 0.217 keV/nm and 0.084 keV/nm for Pd and SiC respectively. Therefore the energy loss of incident Xe ions was via electronic excitation from inelastic collisions and not nuclear elastic collisions.

The overlay RBS spectra of Pd/SiC samples which were irradiated by SHIs is illustrated in Fig. 2. It can be observed that after room temperature irradiation at fluences of 1.07×10^{14} and 4×10^{14} ions/cm^2 no visible changes in the RBS spectra occurred. The spectra of the RT irradiated samples perfectly overlay that of the as-deposited Pd/SiC sample. However, after SHI irradiation at fluences of 5×10^{13} ions/cm^2 at a temperature of 400 °C, intermixing was observed to occur across the Pd/SiC interface. The back edge of Pd peak was observed to have shifted towards the SiC substrate while the Si edge shifted towards the Si surface channel. A step on Si edge was observed to have formed and the RUMP simulations of this sample indicate that a 105 nm wide layer of Pd remained unreacted and an intermixed region of about 50 nm wide had formed between Pd and SiC substrate. This intermixed region had a composition of Pd 67.8 at.%, Si 16.1 at.% and C 16.1 at.% suggesting the presence of Pd_4Si at the Pd/SiC interface.

Phase identification and crystallinity studies were performed by GIXRD analysis of all the Pd/SiC samples. The XRD patterns in Fig. 3 indicated some diffraction peaks of Pd indexed to (111), (200) and (220) planes of the as-deposited Pd thin films. These diffraction peaks indicate the polycrystalline structure of the as-deposited Pd thin films and no silicide phases were present. GIXRD analysis of the Pd/SiC sample after ramped annealing to a temperature of 650 °C indicated that only a single silicide phase (Pd_2Si) was observed to have formed and no Pd phase was present indicating that all the Pd thin film had reacted with the SiC substrate. Pai et al. [12] observed that annealing Pd/SiC samples at 500 °C, only

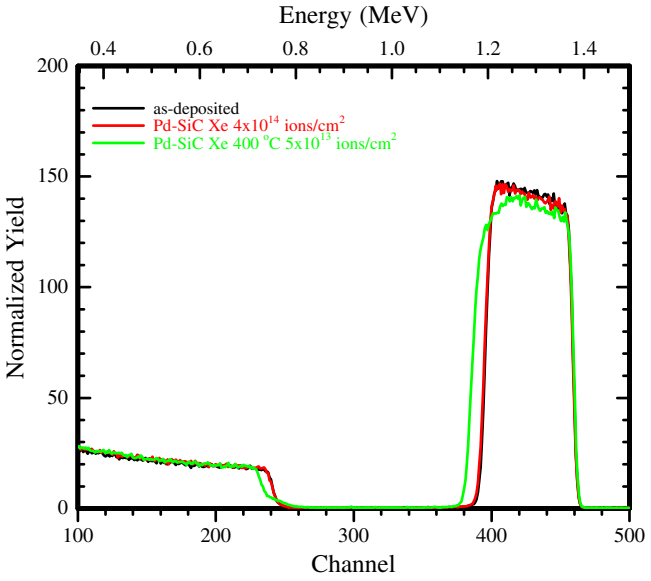

Fig. 2. Overlay of as-deposited Pd/SiC sample and after SHI irradiation at fluences of 1.07×10^{14}, 4×10^{14} ions/cm^2 at room temperature and at 5×10^{13} ions/cm^2 (400 °C).

Pd_3Si formed which gradually converted to Pd_2Si at 900 °C. Pd has been reported not form any carbides when in contact with SiC at high temperatures and only Pd silicides and free carbon form at the interface [13]. The GIXRD results correlate with the RBS observations with regards to the phases formed at Pd/SiC interface and these results agree with previous studies [12,13].

After SHI irradiation at fluences of 1.07×10^{14} and 4×10^{14} ions/cm^2, the XRD patterns were similar to the as-deposited one but an increase in peak intensity with increase in ion fluence was observed to occur. This indicates that the SHI irradiation induced some increase in the crystallinity of the Pd thin film. This observation correlated with RBS results that no diffusion/reaction between Pd and SiC occurred at these ion fluences. The only difference is the appearance of the peak at 2θ position of 72.5° after irradiating at ion fluences of 4×10^{14} ions/cm^2. This peak was indexed to the Pd_2Si (401) phase which formed due to SHI irradiation at this ion fluence. After SHI irradiation at fluences of 5×10^{13} ions/cm^2 at 400 °C, Pd_9Si_2 at 2θ position of 59.8° corresponding to the (106) plane, Pd_4Si (163) peak at 77.1° and Pd_5Si (310) at 34.5° 2θ position were observed to have formed. The XRD patterns from the unreacted Pd of the sample irradiated by SHIs at 400 °C were similar to the RT SHI irradiated ones but the peaks were much broader. This is a surprising result which might indicate that SHI irradiation at this temperature somehow suppresses recrystallization of the Pd thin film. Widening of the Pd peaks could also be an indication of phase transition from one phase to another or a decrease in the grain size in the Pd thin film after SHI irradiation at 400 °C. Hence, GIXRD analysis revealed that SHI irradiation promoted the transformation in the Pd film and led to the formation of new Pd silicides at the Pd/SiC interface.

Although the Pd/SiC interface is stable up to a temperature of 450 °C under thermal annealing, the temperature of reaction can be lowered under Xe SHI irradiation at 400 °C. These reactions occur at a lower temperature due to the combined effects of SHI irradiation and temperature. The initial phases to form in the annealed samples was found by RBS analysis to be Pd_3Si ($Pd_2Si + Pd_4Si$) while the initial phase to form after SHI irradiation was found to be Pd_2Si (401) by GIXRD analysis.

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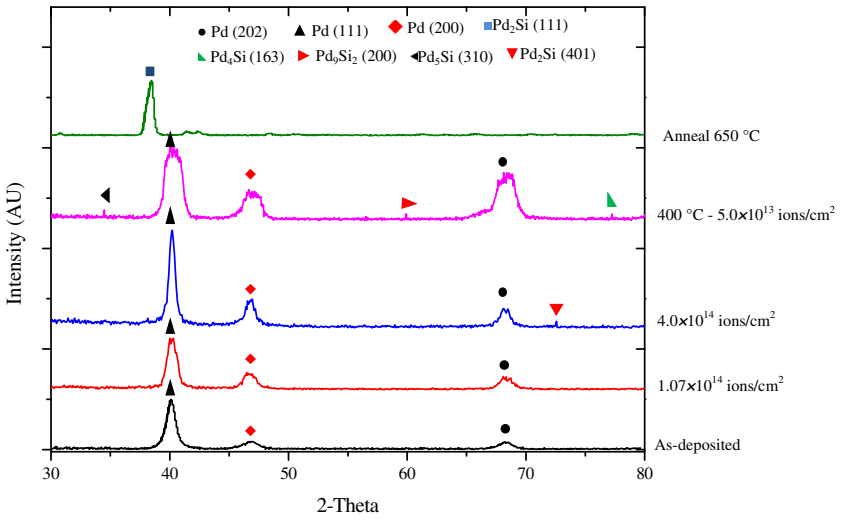

Fig. 3. GIXRD pattern of as-deposited Pd/SiC, after RT irradiation at fluences of 1.07×10^{14} and 4×10^{14}, 5×10^{13} ions/cm^2 at 400 °C and after in situ annealing at temperature of 650 °C.

Two models exists which qualitatively explain the interface intermixing induced by energy transfer from SHI irradiation, these are the thermal spike [14] and the Coulomb explosion models [15]. 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 [16]. This transient temperature spike lasts for about 10^{-12} s [14] and can cause two layers at an interface to attain a molten state, leading to intermixing of atomic species involved.

The reactions that occurred at the Pd/SiC interface can be attributed to thermal spikes due to electronic excitation under high temperature SHI irradiation and multiple ion impacts in the near surface region. This is agreement with the thermal spike model since at high initial temperatures, lower energy is required to melt a material [17]. This is due to the fact that energy necessary to melt a material depends on its initial temperature especially in the case of low melting point materials such as Pd. The interdiffusion observed between Pd and SiC most probably occurs in the hot or molten ion track [18].

4. Conclusion

In this study we have investigated the effect of thermal annealing of Pd thin films deposited on SiC substrates compared to room temperature and high temperature SHI irradiation induced mixing and identified the phases formed. Interface mixing was observed to occur in both cases. Two distinct reaction regimes were observed to occur after annealing above 450 °C and the width reaction zone of the initial reaction varied almost linearly with annealing time. The threshold fluence for compound formation to take place between Pd thin films and SiC with 167 MeV Xe^{26+} ions at room temperature irradiation was found to be 4×10^{14} ions/cm^2 with the formation of Pd_2Si as the initial phase. We demonstrated that further interface mixing or diffusion between Pd and SiC occurred and was induced by SHI irradiation at fluences of 5.0×10^{13} ions/cm^2 at 400 °C as indicated by the RBS and GIXRD analysis. The temperature of initial reaction was lowered from 450 to 400 °C by SHI irradiation due to interdiffusion across the interface during a transient melt phase following the thermal spike model.

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