The effect of thermal annealing in a hydrogen atmosphere on tungsten deposited on 6H-SiC

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1. Abstract

Tungsten (W) film was deposited on bulk single crystalline 6H-SiC substrate and annealed in H_2 ambient at temperatures of 700 ºC, 800 ºC and 1000 ºC for 1 hour. The resulting solid-state reactions, phase composition and surface morphology were investigated by Rutherford backscattering spectrometry (RBS), grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM) analysis techniques. These results are compared with the vacuum annealed results reported in our earlier work. As-deposited RBS results indicated the presence of W and O_2 in the deposited thin film, the GIXRD showed the presence of W, WO_3, W_5Si_3 and WC. RBS results indicated the interaction between W and SiC was accompanied by the removal of oxygen at 700 ºC. The GIXRD analysis indicated the presence of W_5Si_3 and WC in the samples annealed at 700 ºC. At temperatures of 800 ºC and 1000 ºC, W annealed in a H_2 ambient further reacted with the SiC substrate and formed mixed layer containing silicide phases and carbide phases, i.e.W_5Si_3, WSi_2, WC and W_2C. The SEM micrographs of the as-deposited samples indicated the W thin film had a uniform surface with small grains. Annealing at 800 ºC led to the agglomeration of W grains into clusters making the surface rough.

Keywords: tungsten, SiC, interface, reactions, annealing

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2. Introduction

Silicon carbide (SiC) is used in high temperature gas cooled reactors (HTGRs), electronic devices, fusion reactors etc. [1–3]. This is due to its high thermal stability, high thermal conductivity, electric field strength, resistance against aggressive chemicals and abrasion [3–5]. In HTGRs, SiC is used for fuel kernel encapsulation in tri-structural isotropic (TRISO) particles. In these TRISO particles, SiC is the main diffusion barrier for radioactive fission products (FPs) [6], [7]. Failure of the TRISO particle in retaining FPs will lead to the release of the FPs into the primary cooling circuit thus causing danger of contamination to personnel and environment. There are several factors which may contribute to the failure of the SiC in retaining radioactive FPs. These include; thinning of the SiC layer due to reactions with FPs such as palladium (Pa) and zirconium (Zr) and the gas build up leading to a rise in pressure that may exerts strong tensile stress in the SiC and lead to cracks through which the FPs can escape [7–11].

These SiC drawbacks may be improved by enhancing its physical, mechanical, thermal and chemical properties. This can be achieved by adding a coating layer on the SiC layer of the TRISO particle [12], [13]. The use of tungsten (W) as a suggested coating material has good advantages such as a low sputtering yield, inherent heat resistance, high thermal conductivity, excellent corrosion and abrasion resistance [3]. The enhancement of the shielding effect of SiC will play a remarkable role in terms of improving the SiC layer strength. This may allow for higher burn-up and enrichment without causing harm to the structural integrity of the TRISO particle.

Recently, we reported on the vacuum annealing of a thin tungsten layer deposited on 6H-SiC [14]. In this study, we report on the effect of thermal annealing of the same system in hydrogen and the reactions which occur due to annealing. The effect of heat treatment of W-SiC structure in H_2 is an important aspect which has not been studied in detail by other researchers.

3. Experimental Procedure

Semi-insulating 6H-SiC single-crystal wafer of 2 inch diameter, 330 μm thickness, with a micro pipe density of < 10 cm^{-2} and root mean square (rms) surface roughness of < 0.5 nm was used as starting material. The W sputtering target (99.9% pure) was obtained from AJA

International Inc. Thin W film was sputter-deposited on the 6H-SiC wafer by initially mounting the wafer on a rotating sample holder to ensure that a uniform layer was deposited. The base pressure in the chamber was first pumped down to 10^{-7} Torr and then subsequently filled with Argon (Ar) gas to a pressure of 10^{-3} Torr. The Ar gas flow was kept constant at 8.0 SCCM. W target was sputter-cleaned for 10 minutes using Ar plasma before the actual sputtering process was done at room temperature. A thin-film layer of W was successfully deposited on the SiC substrate and the samples were subsequently annealed in hydrogen (H_2) gas of 99.95% purity at 700 °C, 800 °C and 1000 °C for 1 hour in a quartz tube furnace. The flow rate of H_2 gas in the quartz tube was maintained at 250 SCCM.

All the samples were analysed using Rutherford backscattering spectrometry (RBS) before and after annealing. Simulation of RBS spectra was done using the RUMP code [15] to obtain the thickness of the W deposited layer, composition of deposited layer and the reaction zone. The energy used for the He^+ ions was 1.6 MeV with a scattering angle of 165°. XRD analysis was performed using a Bruker D8 Discover XRD system with a Cu K_α radiation source to identify the phases present and orientation before and after heat treatment of the samples. The as-deposited sample was used to determine the angle of incidence with respect to the surface of the X-ray beam. Since the peaks of the single crystalline SiC substrate would much larger than the reaction product peaks and would dwarf them, the angle was reduced from 10° to the point where the SiC peaks just disappeared. The final angle used for analysis was 0.5°. A field emission gun scanning electron microscopy (FEG-SEM) powered with a Zeiss Ultra 55 high resolution field emission microscope was used to study the surface morphology of the samples before and after annealing at the different temperatures.

4. Results and discussion

4.1. Rutherford Backscattering Spectrometry (RBS)

The RBS spectrum of W deposited on 6H-SiC is shown in Fig. 1 and the corresponding simulated spectrum obtained by RUMP computer code is also included. The surface channel positions of the elements in Fig. 1 are indicated by the arrows. The thickness of the deposited W layer obtained from RUMP simulations was found to be 65 nm, which was composed of 65.6 at.% W and 34.4 at.% O_2. This indicates that an oxide layer had form; W reacted with O_2 to form tungsten oxide.
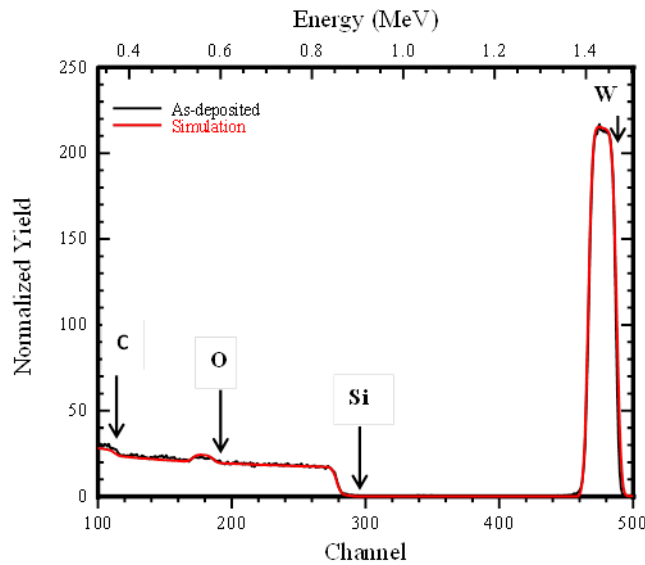
Fig 1: *As-deposited RBS spectrum with the corresponding RUMP simulation.*

The W thin film deposited in 6H-SiC was annealed in H_2 ambient for 1 hour at temperatures of 700 ºC, 800 ºC and 1000 ºC, and the corresponding RBS spectra are shown in Fig. 2. The as-deposited RBS profile has an oxygen peak at channel number 190 while the 700 ºC annealed spectrum has no oxygen peak.

The as-deposited W peak has a lower peak height compared to the 700 ºC W peak. The difference between the two spectra can be explained to be due to the presence of oxygen in the as-deposited layer. The presence of oxygen in W reduced the peak height of the RBS spectrum of as-deposited sample. After the oxygen content had been reduced in the W film, the height of W peak increased as seen in Fig. 2. The increase in W peak height after annealing in hydrogen due to the removal of oxygen, has also been observed by other researchers [16], [17]. The RUMP simulation of the sample annealed at 700 ºC indicated that a reaction had taken place between W and SiC. This resulted in a W layer of 27 nm, with a reaction zone (RZ) layer of 14 nm where the reaction between W and SiC had occurred as a result of the interdiffusion between W, Si and C. The composition of the RZ was obtained using RUMP simulation. The RBS spectrum was simulated with two layers in the RZ in order to have a good fit. The RUMP simulations of the initial layer suggests the presence of W and WC phases with concentrations of about 96.0 % and 4.0 % respectively. In the second layer, the W concentration was found to be 76.5 %, WC is 6.4 % and W_5Si_3 concentration was 17.1 %.

There are two possible explanations for removal of oxygen in the deposited film: first one is, during annealing hydrogen reacts with O to form H_2O according to chemical reactions in equation (1), (2) and (3) [18]:

$$4WO_3 + H_2 \leftrightarrow W_4O_{11} + H_2O \tag{1}$$

$$W_4O_{11} + 3H_2 \leftrightarrow 4WO_2 + 3H_2O \tag{2}$$

$$WO_2 + 2H_2 \leftrightarrow W + 2H_2O \tag{3}$$

The second explanation is that carbon from the SiC reacted with oxygen to form carbon dioxide gas which then flowed out of the system together with the H_2 gas [16]. The more plausible explanation in our case is the latter, i.e. that the H_2 gas reacted with oxygen, leaving a pure W layer. To further investigate whether H_2 reacts with O to form a pure W layer, as speculated above, the W-SiC samples were annealed at 600 ^{o}C (no interaction was expected at this temperature [19]) for 1 hour. The RBS spectrum and RUMP simulation (not shown here) indicated the presence of W with thickness of 30 nm with no oxygen. The loss of W might have been due to delamination. This thickness is of the same order of magnitude as the one obtained after annealing at 700 °C where some W delaminated. No interactions between W and SiC were detected. The RUMP simulations indicate that after annealing at 700 °C, the carbon and silicon concentration in the RZ was almost stoichiometric. This result supports the theory that H_2 reacts with oxygen in the deposited thin film.

A decrease in the height of the tungsten peak after annealing at 800 ℃ was observed indicating further reactions between the W and SiC took place, see Fig. 2. RUMP simulations indicated the presence of C in the W layer. C migrated to the W layer, were it reacted with W to form carbide(s) in the W matrix. Due to this diffusion of C into the W layer the amount of Si present in the RZ nearer to the SiC substrate was higher than that of C. The RZ layer increased to 19 nm and the W layer containing the diffused C increased to 28 nm. The RUMP simulation indicated the presence of tungsten silicide(s) and carbide(s). The reaction of tungsten with SiC resulting in the formation of silicides and carbides at temperatures of 700 ℃ and above has also been observed by other authors [5], [19], [20]. After annealing at 800 ℃ the RUMP simulation suggested the formation of two layers in the RZ similar to 700 ℃, from which the concentrations of present phases in each layer were determined. At 800 ℃, the first layer was composed of 92.4 % of W and 7.6 % of WC. While the second

layer had a concentration of 62.8 % of W, 17.4 % of W_2C, 14.4 % of W_5Si_3 and 5.4 % of WSi_2.

Annealing at 1000 ºC caused a further decrease of the W peak height/yield and a further shift of the W peak to the lower energy channels; see Fig. 2. An increase in C content in the W layer, that is, the first layer from RUMP simulation was observed to occur. This first layer was composed of W with 58.8 % and C with 23.5 % and the thickness of this layer increased to 38 nm. From the RBS spectrum it can be observed that the presence of oxygen and Si at the surface of the W-SiC sample annealed at this temperature. The Si layer observed on the surface most probably came from the Si sample holder used during annealing at 1000 ºC. At this temperature Si sublimation was taking place with deposition of the Si on the W-SiC system. When the sample was taken out of the annealing chamber, exposure to air led to the oxidation of the Si layer. The RUMP simulations indicated that the surface of the samples had a thin layer composed of Si and O_2. The reaction zone obtained from the RUMP simulation at 1000 ºC was also composed of two layers with different concentrations of carbides and silicides in the different layers. Layer one had W, WC, and WSi_2 concentrations of 26.45 %, 47.0 % and 26.55 % respectively. The second layer had concentrations of 10.66 % W, 66.9 % W_2C, 16.32 % W_5Si_3 and 6.12 % WSi_2. The concentrations of the silicide phases (WSi_2 and W_5Si_3)in both layers increased with the increase in annealing temperature. The concentrations of the carbides formed (WC and W_2C) varied with increase in temperature.
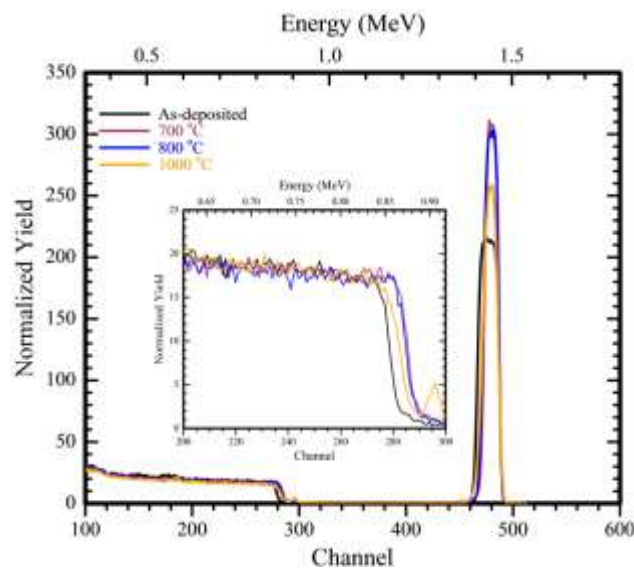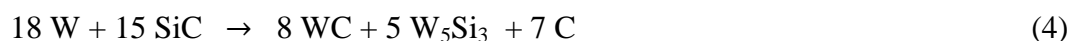

Fig. 2: RBS spectra of the as-deposited and annealed samples in H_2 gas for 1 hour at temperatures of 700 to 1000 ºC.

5. Grazing Incidence X-ray diffraction (GIXRD) results

After RBS analysis, the same samples were examined using XRD at grazing incidence geometry to confirm the RBS results. GIXRD patterns of the W thin film deposited on 6H-SiC before and after annealing are depicted in Fig. 3. The as-deposited pattern had W peaks at 39.89º, 43.91º and 82.15º 2θ positions attributed to (222), (211) and (222) planes respectively, W_5Si_3 peaks assigned to (310) and (512) planes at 29.49º and 61.57º were observed to be present. This implies that W reacted with SiC during deposition resulting in the formation of silicide and carbide. The carbide formed was WC corresponding to (101) and (100) at 2θ position 35.65º and 48.38º respectively. The appearance of WO_3 (112) at the 34.26º 2θ position and WO_3 (111) at the 41.87º 2θ position indicates the presence of an oxide in the as-deposited W film. The latter GIXRD result for as-deposited sample correlates with the RBS results discussed earlier in terms of the presence of oxygen in the W layer.

Annealing the W-SiC samples at 700 ℃ resulted in an increase in the W peak intensities and additional W peaks appeared. The additional W peaks were due to the removal/reduction of WO_3 at 2θ position 35.65º by the hydrogen gas to form a W pure layer. This correlates with the RBS results after annealing the samples where the W peak height increased indicating the removal of oxygen present in the as-deposited W film. The increase in peak intensity of W from the broad peaks on as-deposited sample to the narrow peaks after annealing is due to the change in the polycrystalline nature of our samples to larger crystallites. An increase in the peak intensities of the W_5Si_3 and WC phases was observed to occur and was most likely due to further reactions between W and SiC taking place resulting in the increase in the volume fraction of these phases in the RZ.

Annealing at 800 ℃ resulted in the decrease of the W-rich W_5Si_3 peak intensity and the formation of Si-rich WSi_2 (224), WSi_2 (200) phases and W_2C (610) at the 2θ positions 103.31º, 45.22º and 102.96º respectively. This implies that a fraction of the W_5Si_3 phase reacted with C from SiC to form WSi_2 and W_2C thus resulting in a decrease in W_5Si_3 peak intensity. The possible reactions are represented by equations (4) and (5) below:

$$18 \, W + 15 \, SiC \;\; \rightarrow \;\; 8 \, WC + 5 \, W_5Si_3 \; + 7 \, C \qquad\qquad\qquad\qquad (4)$$

$$4 \, W_5Si_3 + 7 \, C \; \rightarrow 6 \, WSi_2 + 7 \, W_2C \qquad\qquad\qquad\qquad (5)$$

WC (35.65º) peak intensity increased after annealing at 800 ℃ (See Fig. 3.) compared to the 700 ℃ annealing. The increase in the peak intensity at 800 ℃ is due to the increase in the

quantity of WC after further reaction between W and SiC and change in texture of the nature of our sample due to heat treatment.
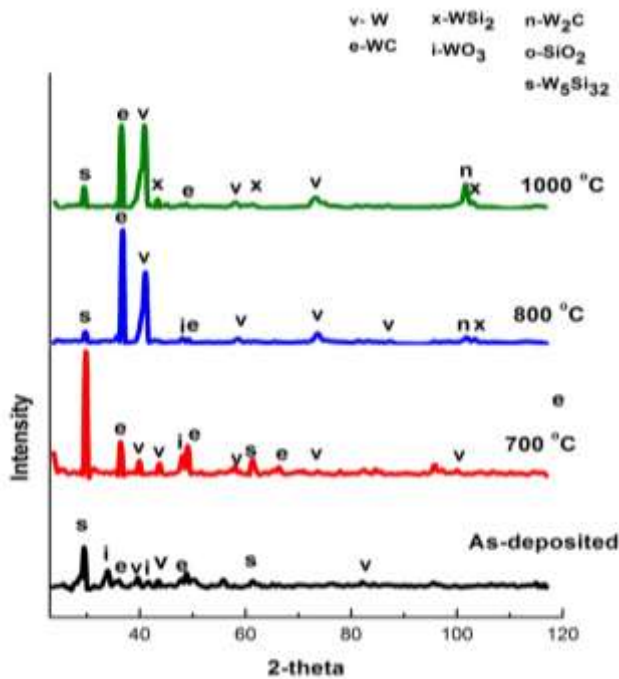

Fig. 3: Grazing incidence X-ray diffraction patterns for W-SiC after annealing in H_2 at 700 ºC, 800 ºC and 1000 ºC.

Annealing at 1000 ºC resulted in an increase in the intensity of the W_2C peak (2θ position 102.96º) compared to the annealing at 800 ºC. Additional peaks of WSi_2 at 42.89º and 62.3º is observed to appear indicating further reactions at the RZ. The W peaks were still present after annealing at 1000 ºC indicating that W layer had not fully reacted. WC (100) peak at position 48.38° increased in intensity after annealing of the sample at 700 ºC as a result of increase in the volume fraction of WC formed at this temperature. The annealing steps from 700 °C to 800°C and to 1000 °C resulted in a decrease in the peak intensity of WC (100) at 2θ position of 48.38°, this was due to transformation of this phase into WC (101). W_2C peaks (102.96º) intensity increased due to the increase in W_2C volume fraction. The WC peak height at 35.65° increases when the samples were annealed at 700 °C, 800 °C and 1000 °C due to increase in the volume fraction and further reactions.

6. SEM Results

Fig. 4 shows SEM micrographs of W deposited on 6H-SiC before and after annealing at 700 ºC, 800 ºC and 1000 °C for 1 hour in H_2 ambient. The SEM micrograph of the as-deposited sample in Fig. 4 (a), shows a fairly uniform surface of the W thin film, with very small grains (almost of the same size) that are evenly distributed. Annealing of the W-SiC samples in H_2 at 700 ºC and 800 ºC for 1 hour led to a marked increase in the size of the grains in line with the XRD results (change in the peak intensity). Consequently, the surface topography of the W-SiC annealed in H_2 at 800 ºC became rougher compared to the 700 ºC annealed sample, see Fig. 4 (b & c). Annealing at 1000 ºC resulted in the formation of hillocks and a much rougher surface compared to the as-deposited. Also present were many small crystallites. The change in surface topography was due to recrystallization of W layer into larger grains and reactions taking place in the W-SiC samples. The SEM results indicate a change in the crystalline nature of the sample surface when annealed at different temperatures; this confirms the causes of the change in the peak intensities in the XRD results is due to change in texture.
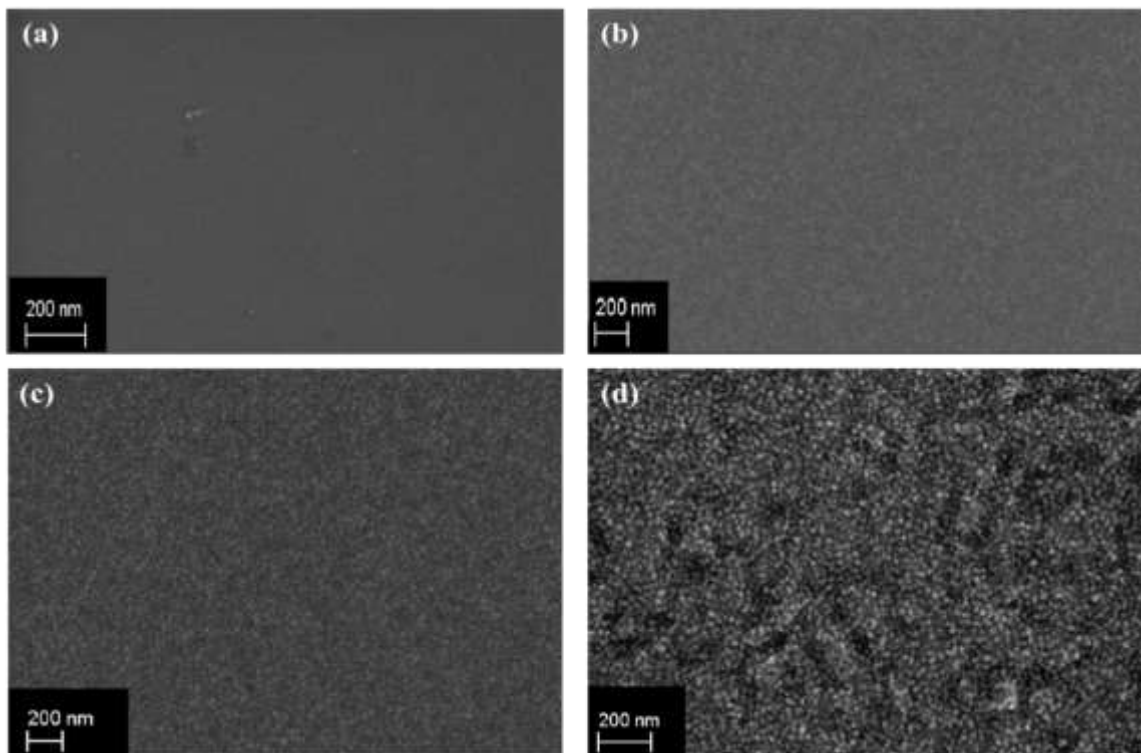

Fig 4: *SEM micrographs of (a) As-deposited W-SiC, (b) 700 ºC, (c) 800 ºC and (d) 1000 ºC for 1 hour annealed in Hydrogen*

The heat of formation for the phases in the W-Si-C system are reported in [21] and the most thermodynamically favoured initial phases to form are WSi_2 and WC. In this study, W_5Si_3 and WC were the initial phases observed to have formed at the W-SiC interface of the as-deposited sample with the thermodynamically favoured WSi_2 only appearing after higher annealing temperatures, i.e. at 800 ºC and above.

The reaction between W and SiC during deposition was also reported in earlier studies done by Geib et al.[20], in which they sputter deposited W on SiC. Their resulting Auger profiles for the as-deposited sample showed that a reaction between W and SiC took place to form WSi_2 and WC. They explained the reaction to be induced by the damage on surface area of SiC. The damage was caused by the cleaning of the substrate surface (in situ by ion milling), thereby weakening/breaking the bonds between SiC. Thus, lowering the amount of energy required to activate the reaction, leading to the reaction taking place during deposition.

In line with the explanation given by Geib et al.[20], the reaction between W and SiC on our as-deposited samples might be due to the Ar plasma cleaning before deposition. The presence of a silicide and a carbide on the as-deposited is due to the favourable kinetic and thermodynamic factors at the interface. It was observed from previous studies that the W films which were deposited on SiC resulted in the formation of W_5Si_3 as the initial silicide [24].

Rogowski et al. [5] reported that the reaction between a W thin film (400 nm) and 4H-SiC after annealing at 700 ºC resulted in the formation of W_5Si_3 and WSi_2 as the initial phases formed. While Baud et al. [19], found W_5Si_3 and W_2C to be the initial phases formed in the reaction between W thin film (500 nm) and β-SiC (CVD) after annealing at 950 ºC. Goesmann et al. [22] [23], had W_5Si_3 and WC as their initial phases which formed as a result of W thin film (150 nm) reacting with 6H-SiC after annealing at 1300 ºC and Geib et al. [20], found WSi_2 and WC to be the initial phases present after RT deposition of W thin film (50 nm) on SiC. In our results the initial phases formed were W_5Si_3 and WC; also observed by other researchers as initial phases, as discussed before. The differences in the phases observed by different researchers are due to the difference in thickness of the W metal layer deposited, deposition method used and annealing temperature.

These H_2 ambient results differ from our earlier work where W was deposited on SiC and annealed in vacuum at 700 ºC to 1000 ºC for 1 hour [14]. The RBS spectrum after annealing at 700 ºC for the vacuum annealed samples had oxygen peak and did not show the changes

(i.e. in peak height and width) as observed in the H_2 annealed samples. The first RBS evidence of a reaction between W and SiC was only after vacuum annealing at 850 ºC. For H_2 ambient annealing at 700 ºC samples, no oxygen was detected and a reaction between the W and the SiC occurred. The GIXRD analysis for vacuum annealing resulted in the formation of carbides (W_3C and WC) as the initial phases, while in the H_2 ambient, W_5Si_3 and WC were the initial phases formed. The formation of W_2C and WSi_2 was observed to take place at 800 ºC for H_2 annealed samples, and for vacuum annealed samples it was observed at 900 ºC, W_5Si_3 was not present for the vacuum annealed samples. Annealing of the W-SiC samples in vacuum at 800 ºC for 1 hour led to the agglomeration of the W grains into islands clusters causing hillocks. The formation of islands on the vacuum annealed samples at 800 ºC might be due to presence of oxides in the vacuum annealed samples, which is relatively high as compared to the H_2 annealed samples.

7. Summary

The interaction of a thin W film on SiC was investigated. The resulting solid-state reactions, phase composition and surface morphology were analysed using RBS, GIXRD and SEM. The samples were annealed in H_2 ambient at 700 ºC, 800 ºC and 1000 ºC for 1 hour. The GIXRD spectra of the as-deposited sample showed that reactions had taken place, with the presence of W_5Si_3, WO_3 and WC. The surface of the as-deposited samples analysed with SEM showed a fairly uniform W thin film, with tiny grains that were evenly distributed. Oxygen from the as-deposited sample was detected on RBS and this was present in the form of WO_3 as observed from the XRD analysis.

The phases identified after annealing at 700 ºC were W_5Si_3 and WC. The XRD patterns for samples annealed in H_2 ambient at temperatures of 800 ºC and 1000 ºC resulted in the formation of WSi_2 and W_2C. Increase in temperature led to the increase in W grain size when annealing in H_2 ambient. Annealing of the samples in H_2 atmosphere assisted in the reduction/removal of oxygen and the temperature of reaction between W and SiC was lowered compared vacuum annealing.

8. Acknowledgement

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