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Solid state reactions between SiC and Ir

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Abstract

Reactivity between SiC and Ir as a function of SiC-crystallinity was investigated by diffusion bonding technique under a vacuum and over the temperature range of 1200-1450°C. As reaction products, various Ir-silicides and free unreacted-C were detected. Reactivity is strongly affected by the temperature and SiC-crystallinity involving a series of interactions, from “no reaction” to “massive exothermic reactions”. In particular, interfacial phenomena are more pronounced by the presence of defects and grain boundaries. Solid state reactions result in formation of fine C-precipitates rearranged in a quasi-periodic microstructure. On the contrary, clustering of highly ordered C-precipitates (C-graphitized) occurs after “massive reactions” take place.

A relationship between the degree of graphitization (from 1 to multi-layers of graphene), temperature and SiC crystallinity was found by Raman spectroscopy. 2D-layering phenomenon is enhanced in polycrystalline SiC at high temperature.

1. Introduction

Technological evolution speeds up exponentially, mainly for electronics. Until now, every advance in electronics was strictly related to the properties of incorporated materials. In particular, many significant steps forward, not only in electronics, were possible because new Silicon (Si)-based materials were improved or ad-hoc designed for increasingly demanding applications. Since electronic devices based on Si-technology reached their design limits in terms of weight, size, efficiency at high temperature and life-time, the

development of a new generation of advanced materials is of primary concern even in enabling emerging technologies.

To this end, silicon carbide (SiC) is a promising candidate in replacing Si, due to its unique properties such as a wide band-gap, high breakdown field, excellent mechanical properties (high hardness and structural stability as well as high resistance to abrasion and erosion), high thermal conductivity, competitive thermal shock resistance and pronounced oxidation resistance [1, 2]. Specifically, if compared with Si, SiC exhibits 3 times wider bandgap, 10 times larger electrical break-down field and 3 times higher thermal stability and conductivity [3]. As practical example, in the unipolar devices such as metal-oxide-semiconductor field-effect-transistors (MOSFETs), the electrical resistance can be drastically reduced when Si is replaced by SiC. In addition, SiO₂ acting as insulator in MOSFETs devices, can be easily layered on SiC substrate surface by thermal oxidation [4]. Moreover, the power and frequency ranges of SiC-MOSFETs are estimated around 1 kV break-down voltage and around 20 kHz switching frequency, then covering the wide requirements for all the common power electronic devices [5].

Currently, the main challenges facing the SiC-based electronic technology are related to produce tailored metal/SiC joint microstructures highly performant in aggressive environments at high temperatures, to deliver the suitable processing conditions for controlling the growing metal/SiC joint interface and finally, to identify the proper joining metal system for each application. In addition, long-term structural, chemical and thermo-mechanical stability of the semi-infinite couple (metal phase and SiC), their microstructures and electrical properties, are the key requirements attesting the reliability SiC/metal joints.

Nowadays, a great interest is gaining the development of electronic devices based on Schottky's currents, in particular those with high heights of Schottky barrier [6]. In order to obtain high heights of Schottky barrier in metal/SiC couples, several metals with high working functions have been investigated, such as Ni, Au and some of the Pt-group elements [7-9]. However, the mentioned metal/SiC joints are not capable to preserve their physico-chemical characteristics at temperatures higher than 450-500°C [10] owing to massive metal atoms diffusion into SiC support.

Despite limited resource availability, Iridium (Ir) is assumed to be the most promising candidate for electronic devices and not only, working over the "conventional" temperatures, due to its relatively high melting temperature of about 2446°C [11]. Owing to the high cost, Ir it is largely unexplored and poorly understood mainly at the liquid state. Nevertheless, from the few studies available in literature, Ir exhibits extraordinary properties. Among these unique features, Ir is a highly corrosion resistant material due to its pronounced chemical stability with limited solubility in other metals and for its well-known low oxygen permeability and diffusivity [12]. For these reasons, Ir is already used as oxygen diffusion barrier and as coating for the combustion chamber in nuclear power plants [13, 14], or as a cathode in advanced super-ignition spark plugs [15]. Ir itself possesses some attractive properties, such as high elastic modulus (516 GPa) and tensile strength (440 MPa) [16], and it is used as as a hardening agent in Pt-alloys and composites designed for jet engine igniters. Moreover, Ir and Ir-silicides show higher working functions than pure Si as reported by [17-19]. Even

when Ir is oxidized, SiC/IrO₂ couple preserves comparable results with the electrical behavior measured at the SiC/Ir joint [20-23].

Around ten Ir-silicides are reported as compounds or intermediate phases [11] ranging from metallic conduction to semiconductors, but not all Ir-silicides are capable to work at high temperatures [24-26]. Depending on the application, the interface microstructure connected with SiC, can strongly influence the final performance of the joint. Consequently, the understanding of interdiffusion and reaction mechanisms occurring between SiC and Ir becomes absolutely crucial. Such knowledge could lead to a guideline for improving metal/ceramic joints by tailoring the interfacial chemistry and its resulting microstructure. This study is particularly fruitful in overcoming one of the limitations in developing SiC-advanced structural applications and metal matrix composites. Indeed, solid state reactions between the SiC-reinforcement and metal matrix may cause interfacial instability degradation of the reinforcement properties, and formation of brittle interfacial reaction compounds during high temperature consolidation as well as during engineering application of the composites.

Such capability in driving bonding mechanisms between dissimilar materials, such as metals and ceramics is crucial in designing active, selective, and stable new more performant catalytic fixed-bed reactors. Indeed, the development of supported heterogeneous catalyst working at more severe conditions, ranks now as one of the key technological accomplishments, making it practical to use expensive catalytic materials in a host of industrial chemical and petrochemical processes. Noble and transition metals appear to make the most active catalysts for many reactions of industrial interest. In this context, the use of SiC/Ir as highly thermo-mechanical resistant couple, allows to extend the life-time of the catalytic reactor even increasing the working temperatures with an evident increasing return.

In this work, an exhaustive experimentally based investigation on the reactivity and interfacial phenomena occurring at SiC/Ir interface, as a function of operating conditions (temperature and starting SiC surface microstructure), in the temperature range of $T = 1200-1450^{\circ}\text{C}$ under a vacuum, applying “diffusion bonding” method, is presented.

As it is well known, solid-state reaction bonding or “diffusion bonding” results may contain errors directly attributable to the nature of the reactants, their surface and presence of impurities (additives, oxide films, etc.). Therefore, the experiments were performed processing high purity raw materials under a vacuum with reduced oxygen content. Moreover, poor adherence at the interfaces in the diffusion zone and accelerated reaction rates due to defects such as cracks, grain boundaries, etc., may also render arduous the right execution of the annealing experiments and the right interpretation of the results. With this aim, two different SiC substrates were selected: commercial hot-isostatic pressed SiC (HIP-SiC) and 6H-SiC single crystal as reference material. In order to relate the obtained microstructures with the actual operating conditions, a careful microstructural characterization was performed by SEM/EDS, XPS and Raman techniques. A deep analysis of all diffusion/reactive phenomena observed within the investigations is reported.

The presence of impurities in the substrate or in the surrounding working atmosphere are typical “technological” problems encountered within the fabrication of commercial joints. To this end, the findings presented in this

paper can be helpful to understand how to tailor the final microstructure and the necessary precautions to use in avoiding unexpected processes.

2. Solid state reactions: experimental procedure

2.1. Materials and sample preparation

The diffusion couples were assembled by placing in intimate contact an Ir rod with a purity of 99.98% (Goodfellows©) (2mm x 2mm) and two different types of SiC substrates: rectangular pieces (with a surface of 25mm²) of HIP-SiC polycrystal (Goodfellows©) and 6H-SiC single crystal synthesized by CVD (Nitride Crystals©). The HIP-SiC is α -SiC without free Si (as confirmed by X-Ray diffraction analysis) and without sintering aids.

With the aim to maximize the contact area, both the surfaces, metal and ceramic substrate, were metallographically polished (800-4000 SiC grinding and 1-0.25 μ m diamond paste) with a final resulting Ra $\leq$ 0.25 μ m and pressed together.

Prior to the diffusion couple assembling, the SiC substrates and Ir were rinsed in an US ethanol bath and dried by compressed air.

2.2. Experimental details: apparatus and procedure

The experiments were carried out in a horizontal induction furnace (see Figure 1), heated by a 800 kHz high frequency generator coupled to a graphite susceptor, detailed elsewhere [27, 28]. The SiC/Ir sample was introduced at the centre of the experimental device and the chamber was degassed under a vacuum ($P = 10^{-4}$ Pa) for 2 hours. The sample was heated up to the testing temperature with a rate of 2°C/s and the achieved isothermal conditions kept constant within the selected dwell time. The temperature was monitored in real time by a pyrometer (Minolta-CYCLOPS52) calibrated by detecting the melting point temperature of several pure metals (Sn, Au, Cu and Ni). Resting on a perfectly levelled substrate, the sample was lighted by an aligned source and within the experiment, its images were captured by a CCD camera (20 frames/sec). The SiC/Ir images recorded were processed by A.S.T.R.A. view® software [29].

Fig. 1. Schematic layout of the a) experimental set-up used and b) SiC/Ir diffusion couple assembling within solid state reaction experiments.

Through a careful determination of the magnification factor, every recorded frame of metal/substrate was processed, redrawing the metal/substrate profile through the mentioned software with a precision of $\pm 1 \mu\text{m}$, for determining the contact angle (θ), base radius (R) and drop height (H). By real-time observation of the sample by CCD camera and post-analysis of the above mentioned geometrical parameters it was possible to follow in great detail the evolution of the solid state reaction by detecting instantaneously any kind of modification occurring in the couple profile. Annealing was performed in the temperature range $T = 1200\text{--}1450^\circ\text{C}$ under a vacuum of 10^{-4} Pa ($\text{PO}_2 < 10^{-7} \text{ Pa}$). The temperature was kept constant for a holding time of 5 hours for “no bonding” to “good bonding” diffusion couples (see Table 1). Instead, in the case of “massive reaction”, where a complete interfacial melting and Ir rod consumption were observed, the annealing time was shortened to 1 hour. After the annealing treatment, the sample was quenched (cooling rate 5°C/s) in order to “freeze” the high-temperature equilibria and resulting interfaces.

2.3. Microstructural and surface characterization

Each sample was embedded in epoxy-resin, cross-sectioned and polished using standard metallographic procedure (800-4000 grinding SiC papers and $1 \mu\text{m}$ polishing diamond paste) and prepared for the microstructural characterization. In order to analyze the microstructure at the interface and the developed reaction zones, the Scanning Electron Microscopy (SEM) was used (Hitachi S3000N) coupled with a X-ray (Bruker) and EDS detectors (XFlash 3001). Moreover, to detect C-molecular morphology, Raman Spectroscopy (Jasco NRS-5100) technique was utilized.

3. Results and discussion

The interfacial phenomena observed in the annealed SiC/Ir (polycrystal and single crystal) samples at different temperatures are detailed in Table 1. In the temperature range of $T = 1200\text{--}1450^\circ\text{C}$, a behaviour evolving from

“no reaction” to “massive reaction” was observed. Interfacial phenomena are strongly influenced by temperature and SiC crystallinity, as expected.

Diffusion couples	Temperature (°C)	Time (h)	Results
6H-SiC/Ir HIP-SiC/Ir	1200, 1300, 1350	5	No bonding (No Reaction)
6H-SiC/Ir HIP-SiC/Ir	1375	5	No bonding (No Reaction) Weak Bonding (Localized Reaction)
6H-SiC/Ir HIP-SiC/Ir	1400	5	Good Bonding (Unconfined Reaction) Partial Bonding (Localized Reaction)
6H-SiC/Ir HIP-SiC/Ir	1425	1	Interfacial melting (Massive reaction)
6H-SiC/Ir HIP-SiC/Ir	1450	1	Interfacial melting (Massive reaction)

Table 1. SiC/Ir diffusion couples and interfacial phenomena observed as a function of temperature; 6H-SiC: SiC single crystal; HIP-SiC: Hot-isostatic pressed polycrystal SiC.

3.1. SiC/Ir reactivity at the solid state

As it can be seen in Table 1, first evidences of interaction between SiC and Ir were observed at $T = 1375^{\circ}\text{C}$, specifically for HIP-SiC at the end of the solid state reaction experiments ($t = 5$ h). Since thin interfacial contours of reaction were observed with limited consumption of HIP-SiC and Ir bar, the HIP-SiC/Ir diffusion couple was effortlessly disjoined at the end of the annealing treatment making possible to analyze by BSE/EDS both the surfaces in contact (Figures 2a, 2b). In particular, by surface examination, spots areas of reaction were identified mainly at the center of the contact area.

Fig. 2. BSE images and EDS map analyses of the contact areas between HIP-polycrystalline SiC and Ir, after solid state reaction experiment performed at $T = 1375^{\circ}\text{C}$ for $t = 5$ h: a) HIP-SiC side surface and b) Ir side surface; map analyses at the related surfaces: c) HIP-SiC and d) Ir.

As it can be seen in Figure 2a, reaction products are adherent to the SiC substrate. Reaction products were identified as a mix of Ir-rich silicides (Figure 2c) and at the perimeter of the reaction front (Ir_xSi_y), a C-enrichment is the result SiC decomposition and C-atoms rejection by the reaction:

As reported in similar works and according to thermodynamics, the reactivity at the SiC/(Me) is mostly driven at the solid state by interdiffusion phenomena [30-35], just to name a few examples. Typically, the more thermodynamically favoured Me-rich silicides respect to SiC decomposition or the lowest melting Me-Si compounds in the Me-rich side of the phase diagram, are the final products. SiC-decomposition as rate-limiting process is extensively demonstrated as well as possible interactions between metal and carbon [36]. Accordingly, Ir reacts easily with pure Si, to form at least 10 different phases with different stoichiometries (see Figure 3), with different SiC-crystalline structures [11, 24, 37, 39] and with SiC-powders at around $T = 1000^{\circ}\text{C}$ [40]. In the latter case, the reactions between SiC powders and Ir evolve at the solid state starting at T

= 1000°C yielding Ir_3Si and C as products, and progressively a two phase of $\text{Ir}_3\text{Si}+\text{IrSi}$ raising the temperature at $T = 1200^\circ\text{C}$. The reaction proceeds completely at $T = 1400^\circ\text{C}$ producing IrSi.

Fig. 3. Ir-Si phase diagram [11].

As demonstrated by [40], Ir does not form carbides and interdiffusion at the C/Ir interface is negligible as documented by [12]. For such mentioned features, the SiC/Ir reaction pathway belongs to reaction mode “type I”, as labeled by Park et al. [36], and the interface microstructure consists of a metal silicides matrix with inclusion of free random or modulated C-precipitates. This reaction mode is basically driven by interdiffusion phenomena with free carbon and silicides as reaction products (see reaction 1). Contrarily, by reaction mode “type II”, the reaction products are typically silicides and binary/ternary carbides.

In agreement with the literature, absence of carbides among the reaction products revealed at HIP-SiC/Ir diffusion couple annealed at $T = 1375^\circ\text{C}$, is confirmed by EDS analysis. In particular, on Ir bar side (Figure 2d), C is mainly detected on the external reacted area (B). On the contrary, at the centre of reaction zone (area A) a Ir_xSi_y phase with higher Ir content is revealed. Focusing on the reaction zone at the Ir bar side (Figure 1b) a teardrop-shaped reaction zone (concave interfacial contour) and dendritic microstructure resulting from the occurred reaction, allow to conclude that, at this temperature, Ir exhibits higher diffusion rate than Si (e.g. higher Ir consumption), thus the kinetics of reaction is affected by SiC decomposition.

Although in the Ir-rich side of the Ir-Si phase diagram, at $T = 1375^\circ\text{C}$, all the Ir-rich phases and compounds are at the solid state, by observing the microstructure, local melting/solidification processes can not be excluded. As distinguished by [30], a massive interfacial melting within a solid state reaction, is caused by low-melting Me-silicide. Whereas, localized partial melting, as in this case, is attributable to large enthalpy of silicides formation (i.e. Ir_3Si and Ir_3Si_2). In addition, Ir-solubility and diffusion coefficients in SiC are very small and the first melting phase encountered in the Ir-rich side of the Ir-Si phase diagram is at $T = 1417^\circ\text{C}$ as documented by [11, 24-26]. As calculated [41- 44], the solid state reactions between Ir and SiC to form Ir_3Si as first and IrSi as final product, are thermodynamically favoured at temperatures higher than $T = 1000^\circ\text{C}$, by

exothermic reactions. However, the Ir and Si interdiffusion rates can be “boosted” through the HIP-SiC grain boundaries (i.e. Kirkendall effect) [38, 39, 40]. The more pronounced diffusion phenomena through defects or grain boundaries can promote local Si-enrichment in the newly formed Ir-silicide compound then moving the actual composition near to off-stoichiometry low melting phases. In addition, the Ir_3Si melting characteristic was detected at $T = 1345^\circ\text{C}$ by [40].

The absence of defects in the 6H-SiC can explain the absence of any interaction phenomena at 6H-SiC/Ir diffusion couple.

Increasing the annealing temperature up to $T = 1400^\circ\text{C}$, after $t = 5\text{ h}$, for both the HIP-SiC/Ir polycrystal and SiC/Ir single crystal samples, two different well distinguished reaction fronts were observed, an “unconfined” planar reaction front along the entire SiC/Ir single crystal contact area (Figures 4a and 4b) and a “localized” concave reaction front for HIP-SiC/Ir (Figures 4c and 4d). As already introduced, the presence of planar reaction zone is basically related to interdiffusion phenomena of Si and Ir. In addition, the absence of grain boundaries at the surface of SiC single crystal in contact with the Ir bar, allows a homogeneous contact between the two surfaces without singularities energetically favoured for enhanced diffusion phenomena. Owing to the mismatch of thermal expansion coefficients of the three layered phases (Ir, reaction products, SiC single crystal) the interface underwent to thermomechanical stress with resulting microcracks (Figure 4b).

Fig. 4. BSE images at the interface of SiC/Ir couples at two magnification, after annealing at $T = 1400^\circ\text{C}$ for $t = 5\text{ h}$: a) and b) 6H-SiC/Ir and c) and d) HIP-SiC/Ir.

Analysing the microstructure and the morphological development of the reaction zone by EDS (Figure 5a), crossing the interface domain from pure Ir to unreacted 6H-SiC substrate, straight interfaces of well-stacked Ir-silicides phases are identified. The sequence is dictated by the corresponding phase diagram.

If the two cross-sectioned diffusion couples are compared, the influence of SiC cristallinity in the morphological development of the reaction zones is evident. It is basically identified by the occurrence of interfacial melting at HIP-SiC/Ir interface (Figure 5b).

Fig. 5. BSE images at the interface of Ir/SiC couples, after annealing at $T = 1400^{\circ}\text{C}$ for $t = 5$ h with included the detected Ir-silicides phases by EDS: a) 6H-SiC/Ir and b) HIP-SiC/Ir.

As it can be seen, irregular interfaces of different single and two phases of Ir-silicides are observed. In addition, the thickness of reaction zone and the end-material consumption are larger than those observed at 6H-SiC/Ir diffusion couple. The detected eutectoid phase $\text{Ir}_3\text{Si}_2 + \text{Ir}_3\text{Si}$ is responsible for the interfacial melting ($T_m = 1417^{\circ}\text{C}$). As documented by [24], the eutectoid reaction also occurs at $T < 1417^{\circ}\text{C}$ because it is in real given by the decomposition of the already formed Ir_2Si at the solid state ($T = 1267^{\circ}\text{C}$). Indeed, Ir_2Si is not revealed by X-Ray diffraction analysis performed on the sample (Figure 6). In parallel, an interesting phenomenon occurring as a consequence of the reaction (1), worthy to be analysed in a devoted section (see paragraph 3.3), is the formation of C as a product, its precipitation behaviour and rearrangement.

Fig. 6. X-Ray Diffractogram 6H-SiC/Ir interface annealed at $T = 1400^{\circ}\text{C}$ for $t = 5$ h.

3.2. Interfacial melting by “massive reaction” at the SiC/Ir interface

If the annealing temperature is raised up to $T = 1425^{\circ}\text{C}$, melting at the interface is observed during solid state reaction experiments performed on both the SiC/Ir diffusion couples, as shown in Figure 7. As shown, the phase transition is easily followed by analyzing contact angle evolution (Figure 7b and 7c). The kinetics of melting varies significantly with the SiC-crystallinity of the substrate. The reaction and melting proceed more rapidly (4 times faster) on the HIP-SiC substrate than on 6H-SiC. As observed in other systems [30-33] and extensively introduced previously, the interfacial melting occurs as a consequence of interdiffusion phenomena and SiC decomposition feeding the reactants to produce Ir-silicides with lower melting temperatures [11]. In particular, both the eutectoid phases, Ir_3Si - Ir_3Si_2 and Ir_3Si_2 - IrSi , show a melting temperature at $T = 1417^{\circ}\text{C}$ and $T = 1425^{\circ}\text{C}$, respectively [11, 24], thus lower or approaching to the annealing temperature selected.

In Figure 8, BSE analyses carried out at both the SiC/Ir couples annealed at $T = 1425^{\circ}\text{C}$ for $t = 1$ h are shown. Owing to the evident interfacial melting, a concave contour of the reaction zone is observed at both the cross-sectioned samples, as expected. As evidenced by BSE/EDS performed at 6H-SiC/Ir, Ir was not completely consumed (see Figure 8a) within the annealing as contrarily occurred for HIP-SiC/Ir, where the solidified drop exhibited a homogeneous Ir_3Si - Ir_3Si_2 microstructure (see Figure 8b). In particular, the unmelted Ir was preserved at the center of the drop and surrounded by a less dense liquid Ir_3Si - Ir_3Si_2 phase as detected by EDS at the top of the solidified drop. In the area adjacent to Ir, the Ir_3Si - Ir_3Si_2 eutectoid phase is present in both cases. Eutectoid phase is still present as a matrix of randomly distributed C precipitates (of about $10\text{ }\mu\text{m}$) at the HIP-SiC/Ir interface. The same C-precipitates were revealed at 6H-SiC/Ir in a matrix of Ir_3Si - Ir_3Si_2 eutectoid phase. The different microstructure development could be explained by the enhanced diffusion phenomena through grain boundaries into HIP-SiC. Adjacent to HIP-SiC, a two phase of Ir_3Si_2 - IrSi , with randomly finer C precipitates (of about $1\text{-}3\text{ }\mu\text{m}$) scattered in the metal phase is detected. Owing to reaction with Si, the Ir_3Si is replaced by IrSi phase as reported by [24, 41].

On the contrary, close to 6H-SiC the reaction zone development consists of well distinguished reaction layers. Immediately adjacent to SiC, a two phase of $\text{Ir}_3\text{Si}_4 + \text{Ir}_3\text{Si}_5$ + randomly dispersed C-nano particles. Moving far from SiC, a layer of IrSi with dispersed C-precipitates with size increasing by increasing the distance from SiC is detected. The Si-enrichment and its higher mobility respect to Ir is evident by the appearance of Ir-silicides products with higher content of Si.

Fig. 7. Evolution of reactivity at 6H-SiC/Ir and /HIP-SiC/Ir polycrystal interfaces during annealing at $T = 1425^\circ\text{C}$ for $t = 1$ h, a) temperature profile, b) contact angle behaviours as a function of time, c) time sequence images during the interfacial melting.

Fig. 8. BSE images at the interface of a) 6H-SiC/Ir and b) HIP-SiC/Ir diffusion couples annealed at $T = 1425^\circ\text{C}$ for $t = 1$ h with high magnification of reaction zones adjacent to Ir and SiC with inserted the outcomes from EDS analyses.

As shown in Figure 9, increasing the temperature up to $T = 1450^{\circ}\text{C}$ (Figure 9a), interfacial melting at SiC/Ir interface was observed on both the SiC substrates.

The complete melting of the metal phase (pure Ir) was observed on both SiC substrates. By following the contact angle behaviours as a function of time (See Figure 9b) and the images sequence reported in Figure 9c, the kinetics of melting, is ten time faster at $T = 1450^{\circ}\text{C}$ in the case of HIP-SiC/Ir (promoted by diffusion at grain boundaries) than 6H-SiC/Ir. Consequently, the melt phase at HIP-SiC/Ir achieves the drop-shape faster than in the case of 6H-SiC/Ir, specifically it consists of a homogeneous drop composition close to eutectoid $\text{Ir}_3\text{Si} + \text{Ir}_3\text{Si}_2$ phase, as shown in Figures 10a and 10b. As already deeply discussed, the phase transition from solid to melting state is given by SiC decomposition favoured by the interdiffusion phenomena of Ir, freshly produced Si and subsequent formed low melting Ir-silicides ($T_m = 1417$ and 1425°C).

Fig. 9. Evolution of reactivity at 6H-SiC/Ir and HIP-SiC/Ir polycrystal interfaces during annealing at $T = 1450^{\circ}\text{C}$ for $t = 1$ h, a) temperature profile, b) contact angle behaviours as a function of time, c) time sequence images during the interfacial melting.

The same eutectoid phase is detected in the substrate as matrix of C-precipitates of 6-10 μm . The C-precipitates size decreases by moving close to SiC. Due to progressive siliconizing (Si-enrichment), from Ir to unreacted SiC, the reaction zone development in the case of annealed 6H-SiC/Ir exhibits the sequence of $\text{Ir}_3\text{Si} + \text{Ir}_3\text{Si}_2$, $\text{Ir}_3\text{Si} + \text{Ir}_3\text{Si}_2 + \text{C}$, $\text{IrSi} + \text{C}$, SiC. The anisotropy of HIP-SiC and the presence of grain boundaries could justify the presence, in the case of annealed HIP-SiC/Ir, of other two low melting ($T \leq 1408^{\circ}\text{C}$ [11]) Ir-silicides, specifically Ir_3Si_4 and Ir_3Si_5 in the reaction zone, resulting probably by the reaction of both Ir_3Si and IrSi with SiC at the solid state and Ir_3Si_2 at the liquid state.

Fig. 10. BSE images at the interface of a) 6H-SiC/Ir and b) HIP-SiC/Ir diffusion couples annealed at $T = 1450^{\circ}\text{C}$ for $t = 1$ h with high magnification of reaction zones adjacent to Ir and SiC with inserted the outcomes from EDS analyses.

3.3. C-precipitation and morphological rearrangement

As aforementioned, when metals are thermodynamically unable to react with C or SiC to produce stable carbides, at the SiC/Me diffusion couple interface, free unreacted C-precipitates are typically detected. In this case, to minimize the interfacial energies, the reaction products, silicides and free C, tend to aggregate themselves through ordered microstructures such as bands or flaky scattered clusters. In addition, the reaction zone development is independent on the cooling rate, as demonstrated by [33], thus its microstructure evolution occurs during annealing and not affected by stress phenomena during solidification. It allows to conclude that the microstructure evolves during the reaction.

The size of C-precipitates, their aggregation, state, topological arrangement in the metal silicide matrix are basically dependent on the properties of the selected metal systems, operating conditions of annealing and C-solubility in the produced silicides phase. In particular, the distribution patterns of C-aggregation and distribution as single or combined random, modulate, alternating layers [30, 31, 33] with varied thicknesses are resulting from a balance of interdiffusion kinetics, rate of SiC-decomposition, rejection of unreacted C, nucleation and growth kinetics of silicides phase [30-34]. Specifically, C-precipitates with a periodic morphology were detected in the reaction zone of SiC/Ni [30-32, 34, 45] and SiC/Pt [30, 33, 34, 46]. Contrary, C-precipitates with different sizes and scattered distribution, were generated in the case of the SiC/Co [34, 46, 47] and SiC/Fe [30, 31, 34] reaction zones.

As it can be seen in Figures 4b and 4d, where the 6H-SiC/Ir and HIP-SiC/Ir annealed at $T = 1400^{\circ}\text{C}$ for 5 h are shown, adjacent to unreacted SiC, a modulated C-precipitation zone is generated. It is composed by alternating coarsened bands of silicides and silicides containing a high density of very fine C-precipitates. Although the reaction evolved in different ways on the two substrates, at the solid state and at the melt phase,

on the 6H-SiC and HIP-SiC, respectively, the similar behaviour might be strictly related to the operating conditions. Diffusion coefficients of the species involved, C-solubility and kinetics of reactions vary significantly with temperature and if the phase is at the solid or at the liquid state. On the other hand, as detected by EDS, Ir-silicides with higher Si-content are present increasing the C-diffusivity in the metal silicide phase. According to the "supersaturation theory" proposed by Wagner [47], during the SiC/Ir reaction process, once a layer of SiC is decomposed, Si atoms diffuse away and react with Ir to form a layer of Ir-silicide (IrSi) in front of rejected C. As a result, the Ir concentration at the SiC reaction interfaces decreases dramatically, decreasing or even temporarily freezing the SiC decomposition. To further decompose SiC, a critical level of Ir concentration needs to be again achieved. In parallel, the dissociated and rejected C-atoms adjacent to the SiC reaction interface, to minimize their interfacial energy, form small clusters and aggregate themselves as a layer. The continuation of this process will give rise to the formation of alternating layers of IrSi and IrSi+C. Moving from SiC to the Ir-terminal, the C-precipitates formed at early stage of the reaction have enough time to further aggregate, grow and randomly distribute in the IrSi matrix.

Increasing the temperature up to $T \geq 1425^\circ\text{C}$, the increased kinetics of SiC/Ir reactions and SiC decomposition, the evident interfacial melting, the increased C-solubility even by the appearance of low melting Ir-silicides matrix phases with increased Si-content (IrSi+Ir₃Si₂, Ir₃Si+Ir₃Si₂, Ir₃Si₄, Ir₃Si₅) might be the factors concurring to the different rearrangement of C-precipitates observed in the reaction zone. In particular, a random C-precipitation zone is generated and the C-precipitates show (see Figures 8 and 10) a size distance-dependence from the SiC reaction front, from nano-sized C-precipitates adjacent to SiC to larger particulates in remote areas. In addition, as it can be seen in Figure 11a, the C-precipitates adjacent to Ir-terminal, exhibit the typical lamellar structure of C-graphitic state. The C-graphitic state was also confirmed by Raman analysis (Figure 11b) by the presence of the three characteristic bands of crystalline C-based materials (graphene and graphite). The results obtained are in good agreement with those reported on SiC/Pt [30-31]. Far from unreacted SiC, the C-precipitates formed earlier, go through a longer heat treatment favouring the C-change from amorphous (typically adjacent to unreacted SiC) to ordered state, as well as the clustering phenomenon resulting in larger C-aggregates.

Fig. 11. Cross-sectioned area adjacent to Ir-end terminal of 6H-SiC/Ir diffusion couple, annealed at $T = 1450^\circ\text{C}$ for 1h; a) HR-BSE image; b) Raman spectrum.

To relate the structure of C-precipitates to the operating conditions and SiC-crystallinity, Raman analyses were performed on all the diffusion couples SiC/Ir annealed at $T \geq 1400^\circ\text{C}$ in the area adjacent to the SiC/Ir starting interface. In Figure 12 the outcomes obtained by Raman analyses performed on 6H-SiC/Ir annealed couples as a function of temperature are collected and shown. As it can be seen in Figure 12a, moving horizontally (for a distance of 30 μm) the Raman detector, transition from graphene (from one to few planes [48-50]) to graphite (multi-layered graphene) are detected on the annealed couples at the temperatures of 1400°C and 1425°C (see Figures 12b and 12d). On the contrary, the Raman spectra performed at higher temperature ($T = 1450^\circ\text{C}$, see Figure 12f) evidenced C-graphitic precipitates.

Fig. 12. Optical microscopy images and linear mapping Raman spectroscopy performed on reaction zones adjacent to Ir-end terminal of 6H-SiC/Ir diffusion couples annealed at a) and b) $T = 1400^\circ\text{C}$, c) and d) $T = 1425^\circ\text{C}$; e) and f) $T = 1450^\circ\text{C}$.

Correlating the 2D and G intensities by the relationship I_{2D}/I_G it is possible to obtain the number of graphene planes. In particular, as demonstrated by [51-53] a I_{2D}/I_G value higher than 1 corresponds to graphene with a number of planes less than 8. Contrary, when I_{2D}/I_G is less than 1, it corresponds to graphite, then a number of graphene layers higher than 8.

In Figure 13a, the value of the intensities ratio I_{2D}/I_G as a function of temperature and SiC-crystallinity are shown. At the lowest temperature ($T = 1400^\circ\text{C}$) an intensities ratio higher than 1 is detected on 6H-SiC/Ir diffusion couple confirming the presence of graphene morphologically layered from mono to less than 8 layers. On the contrary, at the same temperature the appearance of C-graphitized is revealed by Raman spectroscopy at HIP-SiC/Ir interface. As shown in Figure 13b, a general trend of graphene layering exists as a function of temperature. Specifically, the transition from mono/few layers to multi-layers of graphene (graphite) is favoured by increasing the temperature, as expected. In addition, the process is affected by SiC-crystallinity. In particular, the layering phenomenon is enounced (10-15%) in the case of polycrystalline substrate. It could be directly influenced by the higher kinetics of reactions observed on HIP-SiC respect to 6H-SiC where, the absence of defects or grains, in somehow suppress or delay interdiffusion phenomena, SiC-decomposition, nucleation and growth of Ir-silicides, as discussed strictly related to the C-precipitation behaviour and rearrangement, etc.

Fig. 13. Intensity ratio (I_{2D}/I_G) by Raman spectroscopy analysis; a) I_{2D}/I_G mapping and b) I_{2D}/I_G as a function of temperature and SiC-crystallinity.

In particular, as demonstrated by [54-56] the growth of graphene as mono or few-layers at the surface of a molten metal phase, depends strongly on the the quantity of C dissolved in the melt and on the solubility limit of C in the liquid as well as the selected cooling conditions. At the temperatures higher than $T = 1400^\circ\text{C}$, the

presence in the reaction zones of melt Ir-silicides with a higher Si-content, favours the dissolution of higher amount of C, thus the C-solubility limit is achieved slower than at temperatures of 1425°C and 1450°C. In addition, as discussed in the paragraph 3.1, in the 6H-SiC/Ir annealed at $T = 1400^{\circ}\text{C}$, the reactions phenomena evolve almost at the solid state and further suppressing or limiting the C-dissolution into formed Ir-silicides phase.

4. Conclusions

Reactivity of annealed SiC/Ir diffusion couples was investigated as a function of SiC-crystallinity over the temperature range of 1200-1450°C under a vacuum and reduced oxygen content in the surrounding atmosphere.

Reactions at solid and liquid states were observed as a function of temperature. In particular, the interfacial melting was confirmed by the observed non-planar contour of the developed reaction zone. As demonstrated by EDS analyses, the interfacial melting occurred by the formation of low melting Ir-silicides. All the diffusion phenomena were favoured by the presence of grain boundaries in the SiC polycrystalline (HIP-SiC). Temperature and SiC crystallinity are the main factors in determining the transition from “no bonding” to interfacial melting.

Reactions occurring almost at a solid state are responsible for a C-precipitation and rearrangement in a quasi-periodic microstructure. Contrarily, under “massive reaction” conditions, clustering of C-precipitates is favoured. The size of C-precipitates increases by moving far from unreacted SiC and it is more pronounced when Ir-silicides phases with higher Si-content appear as reaction products.

As confirmed by Raman spectroscopy, such C-precipitates exhibit a high degree of crystallinity. According to the results obtained, layered graphene (from 1 to 8 sheets) was detected on 6H-SiC/Ir diffusion couple annealed at $T = 1400^{\circ}\text{C}$. A direct relationship between number of layers, temperature and SiC crystallinity was found. Specifically, increasing the temperature, the number of 2D-graphene layered increases. In addition, under the same operative conditions, the C-layers at the surface of annealed HIP-SiC/Ir is 10-15% thicker than 6H-SiC/Ir diffusion couples.

As introduced, the results presented could be helpful for better understanding the interaction phenomena occurring at the transition metal/ceramic interfaces mainly at the solid state, in fabricating reliable SiC/Me joints capable for working at high temperature and corrosive environments, and in particular in developing a competitive technique in terms of reliability, scalability and low-cost synthesis for growing few-layer graphene or even high quality graphene (single layer) at the interface of metal/ceramic joints or metal matrix composites. In addition, at temperatures up to $T = 1000^{\circ}\text{C}$, the SiC/Ir system exhibits excellent thermo-mechanical response and oxidation corrosion resistance. Such mentioned performances make SiC/Ir joint as ideal candidate in developing advanced electronic devices based on Schottky's current in service over the conventional temperature ranges. For the same reasons, SiC/Ir system might be promising for catalytic reactors in enhancing, by increasing the working temperatures, the efficiency in catalytic combustion and selective NO_x catalytic conversion processes.

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