Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

A perspective on non-stoichiometry in silicon carbide

Abdul Majid^{a,b}

^a Department of Physics, University of Gujrat, Gujrat, Pakistan

^b Office of Research, Innovation and Commercialization, University of Gujrat, Gujrat, Pakistan

ARTICLE INFO

Keywords: Ceramics Silicon carbide Non-stoichiometry

ABSTRACT

The non-stoichiometric ceramics are amazing materials with potential to offer applications that are unachievable by using otherwise ideal stoichiometric counterparts. These materials have contributed in wide areas including superconductivity, optical, magnetic, electronic, structural, mechanical and transport applications. The deviation form stoichiometry in a large number of compounds, though usually avoided, has numerous benefits; by increasing ionic conductivity, offering band structure modifications, causing paramagnetic to ferromagnetic transitions, reducing magnetoresistance, increasing mechanical strength, enhancing electrochemical efficiency etc. Keeping in mind the promising contributions of silicon carbide among family of ceramic materials, this review highlights the implications of non-stoichiometry and its properties. The non-stoichiometry produced unintentionally or purposefully is strongly influenced by synthesis conditions and varies for silicon carbide grown in amorphous, crystalline, polycrystalline polytypes in the form of bulk, surfaces and low dimensional structures. The prospects of tuning the properties of silicon carbide on the basis of fabrication of silicon rich and carbon rich by monitoring silicon to carbon ratio are discussed in detail.

1. Introduction

The antonym to constant-composition-compounds 'Daltonides' is known as 'Berthollides' which refers to the non-stoichiometric compounds. The nonstoichiometric inorganic compounds have gained special attention since the observation of non-stoichiometry in hydrogen-palladium system [1,2]. It pointed out possibility of formation of new stable phases, phase-coexistence, structural evolution etc. upon changing the H/Pd ratio [3]. The deviation from non-stoichiometry, being a defect, is usually unwanted because defects are known to degrade the material's properties. However, it has been observed that, non-stoichiometric compounds, sometimes, offer special properties which are not observed in otherwise perfect solids. For example, due to presence of missing atoms, atoms/ions face comparatively low diffusion barrier and feel liberty to move through the solid. It can benefit in a number of ways, especially in fields related to ceramics, superconductivity, electronics, electrochemical applications etc.

Silicon Carbide (SiC) is a renowned ceramic material that has been found a potential candidate for widespread applications in daily life as well as microstructures, optoelectronics, high temperature, high power, high frequency and radiation resistant devices [4]. The key properties of SiC include high melting point, low thermal expansion, high hardness, resistance against corrosion and wear, high thermal conductivity and semiconducting nature. In SiC, Si and C atoms are connected in strong tetrahedral sp³ bonding of covalent rich character with equilibrium interatomic distance of 1.89 Å. Though SiC is found to have large number of polytypes, the cubic form is called β-SiC (also noted as 3 C) whereas the hexagonal types are known as α -SiC (also noted as 6H as well as 2H). The rhombohedral structure (noted by R) is also found, whereas the mixture of these types produces several other polytypes. The efforts have been carried out to grow stoichiometric SiC however the production of defects is highly likely and the outcome strongly depends upon growth strategy and the parameters involved. The impurities/point-defects are incorporated during synthesis/annealing processes which may result in the removal of carbon or silicon from the surface of the bulk to cause deviation from stoichiometry. The production of point defects may facilitate diffusion of either foreign atoms or host atoms of the material which may cause changes in Si/C ratio in SiC. The changes in the ratio may cause change in stacking sequence which favors formation of a specific polytype. The non-stoichiometry therefore provides a driving force to cause polytypic transformations in SiC.

Like other compounds, SiC offers new functionalities and abundant potential for applications when its Si/C ratio deviates from unity. Despite the availability of rich literature and observation of non-stoichiometry and its impacts on the properties of SiC, no review or book has been yet published to draw attention of the community towards this important phenomenon. This review is written with motivation to provide a perspective on the issues related to deviation from stoichiometry in SiC and its impacts on material properties. In the proceeding

E-mail address: abdulmajid40@yahoo.com.

http://dx.doi.org/10.1016/j.ceramint.2017.10.165

Received 29 September 2017; Received in revised form 18 October 2017; Accepted 24 October 2017 Available online 25 October 2017

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Review article





sections, after introducing non-stoichiometry in other renowed compounds, the phenomenon of appearance of this phenomenon in SiC along with role of synthesis and post-growth conditions are elaborated in detail. Moreover, non-stoichiometry at interfaces, surfaces, grain boundaries and its implications in low dimensional and amorphous SiC has been described in detail. A sections is dedicated to shed light on the applications of the material on the basis of non-stoichiometry. Though, the review is not claimed to be exhaustive but it contains reasonable information and materials to draw attention of the community and produce awareness on a crucial phenomenon of non-stoichiometry in SiC.

2. Non-stoichiometric compounds

The non-stoichiometric metallic compounds are formed due to presence of defects including anion vacancy, cation vacancy, interstitial metal and interstitial anion. It is found in compounds, either due to intrinsic defects or introduced by addition of foreign cations or anions in a doping process, is very small amount. Though, in principle it is detectable but it is not considered non-stoichiometry in general and is regarded merely as point defects. These defects, though in small concentration, leave strong impact on electronics, optical and magnetic properties of the materials, especially on semiconductors. The production of n- and p-type conductivity, spin-polarization, shift in band edges, band structure modifications as well as presence of color centers are consequences of doping and intrinsic point defects in semiconductors. With the technological progress, several experimental methods have emerged to detect the level of non-stoichiometry in semiconductors [5].

On the other hand, the compounds having gross departure from stoichiometry are also prepared and the study related to such materials is an active research area [6,7]. The compounds of Transition metals (TM) and Rare earth (RE) as intermetallic alloys (e.g. NiAs, NiTe, AlZr, TiSn, CeCd, NbB₂) or in the form of and their oxides, sulfides, nitrides etc, (e.g. ZnO, CuO, NiO, TiO, FeO, CeO, WO, CaF₂, CrS, FeS, SiN, ZrN) are renowned stable materials in which gross non-stoichiometry has been observed. The notable deviation from stoichiometry in these compounds has provided opportunity to tailor their properties for different applications.

3. Applications of non-stoichiometry

Despite the extensive scientific interests to synthesize defect free ceramic materials, stoichiometrically imperfect compounds have exhibited their worth at several technological fronts. The deviation from stoichiometry appears to modify the material's properties and sometimes introduced new functionalities which are not obtained by using otherwise perfect counterpart of the material. The defects related to non-stoichiometry produce pathways to the ions in otherwise perfect lattice which results an increase in ionic conductivity of the material [8]. An increase in conductivity by seven orders of magnitude has been observed when gallium oxide turned to be non-stoichiometric GaO12 [9]. The changes in electronic band gap in non-stoichiometric V_2O_3 have been observed from 0.2eV to 0.75 eV by changing V/O ratio produced during oxidizing and reducing conditions of sample preparation [10]. The effects of deviation from stoichiometry on para- to ferro-electric transition have been studied in case of BaTiO₃ [11]. It was observed that the transition temperature and the enthalpy of transition varies inversely with Ba/Ti ratio in the samples. The measurements indicated that solid solubility limit, while observing the behavior of solid solution, is higher in case of Ti rich when compared to that of Ba rich case (Fig. 1).

A transition from insulator to metal has been observed when gallium oxide was transformed into non-stoichiometric $GaO_{1.2}$ [9]. The highly large magnetoresistance of 3100% as recorded for stoichiometric layered WTe₂ was observed notably reduced to a value of 71% in case



Fig. 1. Differential scanning calorimetry results recorded for non-stoichiometric BaTiO3 at various Ba/Ti ratios (a) In Ba-rich and (b) Ti rich regimes [Printed with permission from AIP License, Ref. [11]].

of non-stoichiometric material WTe_{1.8} [12]. The deviation from stoichiometry has shown strong impact on electrochemical processes. It has been observed that the catalytic activity recorded for stoichiometric LaFeO₃ consistently increases for series of non-stoichiometric compounds $La_{1-\varepsilon}FeO_{3-1.5\varepsilon}$ [13]. The electrochemical efficiency of nonstoichiometric metallic oxides in perovskite, pyrochlore, olivine structures has been found superior as compared to that of noble metals [14].

4. Non-stoichiometry in silicon carbide

Like several other compounds, the understanding that SiC is useful, if and only if, it is stoichiometric has changed over the years. The technological development of synthesis techniques and characterization tools have played vital role in this regard. It has been observed that chemical vapor deposition (CVD) processes produces Si rich whereas molecular beam epitaxy (MBE) technique offers production of either Si or C rich SiC [15]. The non-stoichiometry in SiC is introduced by point defects including C and Si vacancies, C and Si antisites or Si and C interstitials. In case of low concentration of these defects, SiC retains its structure and lattice parameters but upon introduction of gross deviation of stoichiometry, the structural deformation and phase transformation are most probable [16].

The deviation in stoichiometry is basically measured in terms of Si/ C ratio which is unity in case of absolutely stoichiometric SiC. The ceramic fibers obtained from SiC has widespread applications and the properties of these fibers strongly depend upon synthesis conditions. The first generation of these fibers was found non-stoichiometric due to high carbon content and presence of oxygen [17]. The non-stoichiometry in SiC has caused lowering of absorption coefficient and increase in threshold of optical damage which can be exploited for high power and high field applications [18,19]. The physical properties of SiC have been found strongly dependent on Si/C ratio of the material. The measurement of optical properties of a series of amorphous SiC samples indicated that the value of optical band gap widens with increase in carbon content of the material [20]. Furthermore, the measurements of exponential absorption edge indicated variation in optical characteristics and an increase in Urbach energy with increase in carbon content in Si_xC_x samples.

The stability of single phase SiC has been studied by coarsening of its powder at 2400 °C [21]. In order to investigate the defects and the limits, and effects of non-stoichiometry in the material, the samples having high Si as well as high C ratio were prepared. The structural analysis indicated that Si rich samples were found 3 C whereas the C rich samples were having 6 H polytypes. On the basis of measurement of unit cell volume, molecular weight, density and Si/C ratio within accuracy level of 1%, it was declared that the samples with both polytypes are stoichiometric. It was pointed out that native defects are primarily vacancies, interstitials and antisites with formation energy of any defect pair larger than 3 eV.

Tai et al. prepared amorphous Si_xC_y films by using precursor comprising of different concentrations of argon diluted CH_4 and SiH_4 in a plasma enhanced CVD reactor [22]. The fluence CH_4/SiH_4 was changed from 70% to 40% in order to change the Si/C ratio in the samples and the modification in emitting color was monitored in order to investigate the effects of non-stoichiometry on phosphor properties of the material. The photograph of the films grown at different values of fluence are given in Fig. 2. It was concluded that the films can be used as solid-state phosphor able to produce intense light covering a broad and tunable emission from visible to about 200 nm. It was observed that, upon changing the fluence from 40% to 70%, the concentration of silicon decreases from 70.9% to 58.6% and concentration of carbon increases from 25.5% to 36.7%.

4.1. Role of synthesis conditions in stoichiometry

The thought that, whenever grown, SiC should be stoichiometric in nature, changed as a result of several studies. The properties and stoichiometry of any material strongly depends upon synthesis conditions.



Fig. 2. Photographs of the amorphous non-stoichiometric Si_xC_{1-x} films deposited on Silicon by using fluence ratios of (a) 40%, (b) 50%, (c) 60%, and (d) 70%. [Printed with permission from RSC License, Ref. [22]].

Honorato et al. deposited SiC on pyrolytic carbon layer and discussed the effects of experimental conditions on stoichiometry and mechanical properties of the material [23]. The samples were grown in CVD reactor by using precursors methyl-trichloro-silane (MTS) and graphite by varying the parameters including MTS concentration, deposition temperature and other reactants. It was observed that selection of the parameters strongly affects the stoichiometry of the coating from SiC + Si to SiC and to SiC + C. The temperature dependent investigations indicated that SiC + Si is obtained below 1500 °C which switched to stoichiometric SiC upon increase in temperature. However, upon further increase in temperature above 1500 °C the coating became nonstoichiometric in the form of SiC + C. The usage of propene in the reactants however prevented the appearance of access silicon and caused stoichiometry in the composition even at low temperature of 1300 °C. This study pointed out flexibility of deposition recipe to tune the stoichiometry of SiC which may be exploited for different applications.

Cheng et al. have reported plasma enhanced CVD deposition of Si_xC_{1-x} films of quartz with different C/Si ratio by monitoring the fluence of precursor gases SiH₄ and CH₄ [19]. The changes in fluence (CH₄/CH₄+SiH₄) strongly affected the deposition rate and physical properties of the films including the stoichiometry. The C/Si ratio was observed to change from 0.51 to 1.83 when the fluence ratio was increased from 0.7 to 0.92. It was observed that, at low deposition temperature, SiH₄ molecules decompose quickly which is likely to contribute to non-stoichiometry in the material. Upon increasing the fluence, molecular dissociation energy is reported to decrease which reduces the decomposition rate of SiH4 to cause decrease in concentration of Si in the films. The fluence changes thus provide an environment to add extra number of deficient atoms which resulted in Si or C rich non-stoichiometric films having a specific C/Si ratio. The photograph of semi-transparent films of stochiometric, S rich and C rich SiC is shown in Fig. 3. The deviation from stoichiometry is observed to strongly affect the optical properties of the material. The optical band gap of the films was observed to increase from 1.81eV to 2.50 eV when film stoichiometry was changed from Si to C rich conditions respectively, as shown in Fig. 3(b). The deviation of band gap from its value of 2.1 eV (stoichiometric sample) is due to the fact that excess C atoms



Fig. 3. (a) Photograph of stoichiometric and non-stoichiometric SiC films (b) Optical absorption coefficient measured for stoichiometric and non-stoichiometric SiC films [Printed with permission from RSC License. Ref. [19]].

aggregate to graphite and diamond polytypes. Since both the graphite and diamond exhibit different behaviors in trend of band gap modifications, the changes in band gap of Si_xC_{1-x} was explained on basis of variations of C contents in the films.

4.2. Applications of non-stoichiometric SiC

The silicon rich Si_xC_{1-x} films have been prepared by using Silane rich environment in a low power plasma-enhanced-CVD reactor [24]. The variation in value of RF power of the plasma appeared to tune the silicon molar ratio to produce the series of the material having different Si/C ratio. The films Si_xC_{1-x} presented an enhanced absorption in 400–600 nm region whereas, the values of the band gap were recorded in range 2.05–1.49 eV. Furthermore, the performance of the material was also tested for photovoltaic devices which indicated enhancement of efficiency, reduction in series resistance and increase in shunt resistance upon reducing the film thickness. The Si-rich SiC thin films presented an enhanced absorption in visible region of electromagnetic spectrum showing potential of the material for the devices.

The preparation of SiC ring-wave-guide resonator for use as dataformat-follower and invertor has been reported [25]. The material was deposited on Si wafer coated with SiO₂ in plasma-enhanced CVD reactor by using argon-diluted-silane and methane as precursors. The gaseous composition of the precursors was adjusted in such a way that atomic concentrations of Si and C were 64.3% and 27.1% which gives the final product as non-stoichiometric SiC_{0.42}.

In order to test the effects of sintering on stoichiometry of SiC, the samples in the form of powder have been prepared by high temperature reaction of silicon and graphite [15]. The Si/C ratio acceded stoichiometric composition due to evaporation of Si atoms during high temperature synthesis of powdered SiC samples. The as-prepared samples in the form of agglomerated powder were sintered at high pressure using hydraulic press. The sintered samples were found free from stacking faults, containing low diamond content and exhibited a decrease in lattice constant. The decrease in lattice parameter when compared to its known value points to presence of higher carbon content in the samples. The observed non-stoichiometry was assigned to detection of sp³ type C-C bonds related to C_{Si} in the synthesized SiC powder.

The phenomenon of non-stoichiometry in SiC, keeping growth conditions into account, can be modeled using first principles methods. Density functional theory (DFT) based calculations have been carried out to examine the influence of stoichiometry on the growth mechanism by considering geometry and electrical properties of 2H-SiC [26]. The authors of this work used self-consistent charge based tight-binding DFT (SCC-DFTB) technique to study the surfaces (1010) and (1120) of the material by considering slab models. It was found that the surfaces under stoichiometric conditions are semiconducting, whereas some non-stoichiometric reconstructions are metallic like. In order to produce non-stoichiometry, all Si (C) atoms in top layer was replaced by C (Si) atoms to make the material as C-terminating (Si-terminating). The Si terminating surface was found stable over wide range because Si-Si bond is longer than Si-C bond due to which Si dimmers are more tightly buckled. On the other hand, the C terminating surface happened to be stable only under carbon rich conditions. The Si terminating surface, exhibiting a silicon related state at 0.5 eV above valance band maximum (VBM), appeared to be metallic in nature. On the other hand, the C terminating surface exhibited a carbon related state at 2.9 eV above VBM appeared to be semiconducting in nature.

4.3. Non-stoichiometry at interfaces

The dependence of stoichiometry on growth conditions has also been tested in case of interfaces involving SiC heterostructures. In order to produce metal-oxide-semiconductor (MOS) heterostructures, Chang et al. oxidized the nitrogen doped 6H-SiC samples by annealing at

different conditions [27]. The processing of the samples caused formation of SiO₂ layer on the surface of SiC. Though, the top layer SiO₂ was found stoichiometric but a transition layer SixC formed at the interface of the structure was non-stoichiometric. The interfacial layer was silicon rich (having x > 1) and its thickness was found proportionally dependent on the oxidation temperature. The electrical properties and density of interfacial states in the structure SiO₂/SiC as a function of annealing/oxidation and other conditions were also discussed in detail. In order to explore the microstructure and atomic level picture of SiC/SiO₂ interface, Wang et al. studied, theoretically and experimentally, the effects of hydrogen [28]. The hydrogenation was studied by adding hydrogen to the dangling bonds of Si at top of SiO₂ and to C atoms in the bottom layer of SiC. It was shown that the density of interfacial defects decreases upon nitridation and hydrogenation. The passivation of carbon dangling bonds by H₂ and the passivation of correlated carbon dangling bonds by monoatomic H was predicted on the basis of theoretical calculations. It was further revealed that the interface could be best described in the form of Si-C-O bonded interfacial layer. The three-fold coordinated carbon atoms in the interface were held responsible for the defect states in the interlayer.

Another effort to study this interfacial transition layer has been reported for the structure $SiO_2/4H$ -SiC which was prepared by thermal oxidation of nitrogen doped N-type 4H-SiC [29]. It was observed that the heterostructure comprises of nanoscale layers on both sides of the interface whereas the top layer of SiC was found partially amorphous. Moreover, ternary phase comprising of Si, C and O was formed during thermal oxidation of the structure. TEM images of the sample exhibited one transition layers of thickness 5 nm on SiO₂ side and another transition layer of thickness 3 nm on SiC side of the heterostructure. The ratio of thickness of the two layers was found 0.6. The interfacial layer was non-stoichiometric having C/Si ratio of 0.6 whereas this ratio became zero at depth of 4 nm into SiO₂. Monitoring this ratio indicates that non-stoichiometry prevails to 4 nm depth of SiC. The non-stoichiometry takes place during oxidation process which is likely to release Si atoms to produce silicon vacancies and hence C-rich SiC.

The analysis of the interfacial region is very important because trap centers formed in this region may reduce the carrier mobility and restrict the performance of MOS field effect transistor. Biggerstaff et al. has also studied this interfacial layer to study the effect of this layer on carrier mobility in the heterostructures [30]. The carbon rich non-stoichiometric transition layer was formed on SiC side in such a way that the channel mobility appeared to be inversely proportional to thickness of this layer. In order to probe any possible formation of artificial transition layer in the MOSFET, five different samples were prepared by changing experimental conditions including/excluding the usage of post-oxidation of NO annealing and Al ion-implantation. The analysis indicated that the formation of the carbon rich transition layer is not result of some specific synthesis condition but it is an inherent characteristic of SiC/SiO₂ interface.

In order to explore the origin of formation of carbon rich transition layer in SiC/SiO₂ interface, the potential of first principles calculations may be utilized. The possible reasons of the formation of the nonstoichiometric layer may be interstitial carbon C_i, carbon antisite C_{Si} or their combination. However, the formation of antisite Csi upon transferring an interstitial carbon atom to a Si site thereby kicking it to some interstitial site as Si_i is less probable due to being energetically expensive. Shen et al. carried out quantum molecular dynamics simulation to investigate the mechanism of formation of the transition layer [31]. The authors of this work simulated a 256 atoms supercell of 4H-SiC having 22% excess carbon atoms in the form of random C-C dumbbells with one atom as Ci and the other atom at its specified lattice site. The results of simulation indicated formation of a large complex which revealed the carbon segregation whereas silicon atoms almost remained located on their sites. The initial structure showing only the dumbbells and the resulting structures obtained after MD runs for 6 ps heating up to 1200 °C (and constant temperature run for 18 ps) and



Fig. 4. MD simulations carried out on SiC under different conditions (a) The initial structure showing only the dumbbells (b) The post-simulation structure obtained after MD run for 6 ps heating up to 1200 °C followed by constant temperature run for 18 ps (c) The post-simulation structure after MD run for 2 ps at 2200 °C followed by constant temperature run for 18 ps. [Reprinted with permission from AIP License. Ref. [31]].

then for 2 ps at 2200 $^{\circ}$ C (and constant temperature run for 18 ps) are shown in Fig. 4. The authors concluded that at low carbon concentration, the formation of di-interstitial carbon atoms takes place. On the other hand, at high carbon concentration, accumulation of carbon atoms to form clusters takes place which is followed by migration of silicon atoms away to produce non-stoichiometry in the interfacial region.

In order to further explore the structure of the carbon rich transition layer in SiC/SiO₂ the depth profiling of the structure have been carried out by using medium energy ion scattering (MEIS) [32]. The n-type 4H-SiC was oxidized to produce oxide layer of 200 Å thickness, annealed in NO environment and then etched to obtain a 50 Å thick oxide layer. The depth profiling of the samples was carried out by using 100 keV beam of H⁺ in channeling configuration by directing it along < 0001 > axis of SiC. This report has added into controversy by declaring that the interfacial layer does not contain excess carbon and Si-C-O as well as Si-C-O-N are not observed. However, as per experimental details used in this study, the availability of excess carbon with concentration less than

$1.8 \times 10^{14} \, \text{cm}^{-2}$ was not ruled out.

4.4. Etching induced non-stoichiometry

The study, removal strategies and exploitation, of defects in the bulk, surface or interfaces of SiC related structures is an important research area when technological applications of the material are taken into account. The point defects are unwanted, though they are sometimes useful, but three-dimensional voids are certainly harmful defects and severely degrade the material's properties by applications point of view. The formation of voids in SiC, takes place due to inefficient nucleation and networking of pores, is highly likely [33]. There have been several strategies to prevent from the formation of voids or elimination of available voids in SiC crystals, but hydrogen etching is found very resourceful tool for the purpose [34]. Sander et al. has reported the effects of hydrogen etching on surface morphology of 6H-SiC (0001) carried out by using a CVD reactor [35]. Their investigations pointed to dissimilar etching behavior of SiC when observed inside and outside the hexagonal voids. The etching of flat regions present outside the voids appeared to leave the material's surface stoichiometric due to removal of Si and C in equal concentrations. However, on the other hand, etching of material's regions inside the voids appeared to produce nonstoichiometric material having high Si concentration. The selective removal of C from bottom of the voids was interpreted by taking diffusion constant of reaction products and transport mechanism into account. Considering Kundsen diffusion, hydrogen gas on the flat region and partial pressures of Si and C are at equilibrium which warrants their identical etching and hence stoichiometric reconstruction of the surface. On the other hand, inside the void diffusivity of species is not same and depends upon molecular weight due to which lighter specie, i.e. carbon, faces preferential removal which causes the non-stoichiometry in the favor of silicon. This preferential etching has special consequences in terms of material's properties and can be exploited for device grade applications [36].

4.5. Non-stoichiometry in amorphous SiC

Amorphous SiC due to its distinctive properties offers applications in (resistive, protective, antireflection) coating, passivation, sensors, microelectronics, optoelectronics, telecommunication, medical etc [37,38]. The synthesis of SiC in amorphous phase is carried out by suitable selection of growth conditions. A number of research efforts describing the effects of growth parameters and synthesis techniques on the production of amorphous SiC appeared in literature.

The preparation of hydrogenated SiC films in amorphous phase by using plasma synthesis technique has been reported [39]. The precursor in the form of hydrogen diluted silane along with methane plasma was utilized to deposit carbon rich SiC:H amorphous films on different substrates including crystalline silicon, corning glass and fused silica. The dilution with hydrogen played important role in production of carbon rich films having high band gap, stronger photoluminescence and good photo-electronic properties. The deposited films presented high band gap with values up to 3.3 eV. The annealing behavior of the films was found dependent on composition. The annealing at high temperatures exhibited silicon crystallites in silicon rich films and graphite clusters in carbon rich films. The FTIR results indicated that the frequency of Si-C and Si-H bands increases upon increase in carbon content in the films. Another report on production of amorphous SiC:H films having variable stoichiometry is found in literature [40]. The films with C/Si ratio of 1 and 5 were deposited on silicon substrate by using methyl-silane, phynyl-silane, helium and hydrogen as precursors in plasma enhanced CVD chamber. In order to test the sensitivity of the material to moisture assisted cracking, the fracture properties of the films were tested. These properties were examined by monitoring the transition from cohesive to adhesive fracture and the values of cohesive energy were studied as a function of density. The films exhibited low



Fig. 5. Fracture energy versus density measured for stoichiometric and non-stoichiometric a-SiC:H films. [Printed with permission from Elsevier Publishing, Ref. [40]].

sensitivity which was assigned to the formation of Si-O-Si bonds via hydration and the condensation at SiH_x .

The plot of measured fracture energy versus density for stoichiometric and non-stoichiometric a-SiC:H films is shown in Fig. 5. It can be observed that transition from cohesive to adhesive fracture takes place at density of 1.63 g cm^{-3} . Furthermore, the value of cohesive energy was found proportional to the density in case of stoichiometric films. On the other hand, non-stoichiometric films having low density exhibited deviation from the standard trend and shown very high cohesive fracture energy when compared with organo-silicate and silica glasses [41,42]. The increase in cohesive fracture energy was interpreted in terms of crack-tip-plasticity and dependence of fracture energy on thickness of films.

The same group has investigated the possibility of tuning of plasticity in non-stoichiometric amorphous hydrogenated SiC with C/Si ratio of 5 [43]. They assigned the plasticity in the films to sp^3 hybrid chains CH_x which has been added into glass via decomposition of precursors. The plasticity was controlled by varying the content of phenyl porogen in the films whereas it was found that the involvement of plasticity to cohesive fracture strength depends upon molecular structure of the chains. The observation by changing the number of the chains pointed out that the cohesive fracture energy varies inversely whereas yield strength changes in direction proportion to porogen concentration in the precursor.

Fraga et al. has reported the preparation of non-stoichiometric amorphous Si_xC_y on silicon substrate in a PE-CVD reactor by using SiH_4 and CH_4 gases as sources of Si and C respectively [44]. The films were deposited by varying SiH_4 flow rate 1–4 sccm) and fixing CH_4 rate (20 sccm) in order to ensure non-stoichiometry in the favor of carbon (i.e. x < y). The increase in the ratio SiH_4/CH_4 promoted the silicon content in the carbon rich films. The study of plasma etching of the films was carried out in the presence of mixture of SF_6 and oxygen gases which indicated an increase in etch rate with increase in oxygen content in gas mixture. The etch rate was observed reduced when carbon content in the deposited films was higher with indicates resistance of carbon rich SiC against etching [40]

4.6. Non-stoichiometry in low dimensional SiC

Tello et al. have utilized atomic force nanolithography to restrict electrochemical reaction in nanometer-sized ethanol meniscus which produced nano-bridge [45]. After formation of the nano-cells, electric field migrate the ethanol molecules to silicon where electrochemical reaction takes place to produce carbon rich SiC nanostructures. This method has been developed to produce nanometer-sized carbide structures by utilizing the formation of electric field driven ethyl alcohol nanometer-sized bridges. The production of carbon rich SiC/H with stoichiometry 2.5:1 could be either due to formation of carbon rich termination surface or due to substitution of H on Si sites. The chemical reaction involving the production of carbon rich SiC nanomaterial having stoichiometry parameter x was described as;

$$Si + \frac{x}{2}CH_3 - CH_2OH \rightarrow SiC_x + xH_2 + \frac{x}{2}H_2O$$

The investigation of dielectric properties of Si rich non-stoichiometric SiC nanoparticles has been reported [46]. The samples in the form of powder were synthesized by using laser pyrolysis technique and annealed at different temperatures. The dielectric and impedance measurements of the samples were carried out in widespread range of frequency and temperature. The EPR measurements revealed that the nanoparticles have reactive surface owing to availability of dangling bonds. In order to obtain the non-reactive surface, carbon terminated SiC nanoparticles should be realized. The measurement of electrical properties of the samples revealed an increase in dc-conductivity when annealing temperature was increased. The polarization at the surface was found whereas the EPR electronic centers appeared to contribute to reduce the polarization strength.

The study of intrinsic defects in SiC nanoparticles, prepared by using carbon and active silicon, have been conducted by using electronparamagnetic-resonance (EPR) and pulsed-electron-nuclear-double-resonance (ENDOR) spectroscopies [47]. The measurements revealed four paramagnetic centers with g-values of 2.0043, 2.0029, 2.0031 and 2.0037 which were assigned to carbon vacancy in α -SiC, carbon vacancy in β -SiC, carbon dangling bonds in C-rich phase and three-fold coordinated silicon atom in Si-Si₂N bond respectively. The analysis of microstructure of SiC nanoparticles and EPR measurements helps to explore the intrinsic defects available in the crystalline phase of the material. The stabilization of carbon rich phase involves dangling bonds whereas crystalline phases are monitored by charged vacancies.

5. Summary

The deviation from stoichiometry in compounds is often observed and is strongly dependent upon synthesis and post-growth processing of the materials. The non-stoichiometry appears to modify materials properties in terms of manipulating conductivity, inducing spin polarization, engineering of band gap, optical and electronic properties. This phenomenon has often been observed in SiC owing to its large number of polytypes and offers tailoring of its properties for devices and other applications. The non-stoichiometric SiC has been found offering good mechanical properties thereby exhibiting high resistance against cracking and fracture along with transition from adhesive to cohesive energy. The etching produces deviation from stoichiometry whereas this phenomenon has strong impacts on interfaces and low dimensional SiC. Despite, synthesis and utilization of SiC for several decades, the phenomenon of non-stoichiometry in this material has not been properly understood and offers challenge to the community to explore the basic mechanism responsible for it. The absence of established knowledge on non-stoichiometry in SiC restricts full utilization of this material for applications.

Acknowledgement

Higher Education Commission of Pakistan is acknowledged for providing financial support vide 6509/Punjab/NRPU/R & D/HEC/2016 to execute this work.

References

L.J. Gillespie, F.P. Hall, The palladium-hydrogen equilibrium and palladium hydride, J. Am. Chem. Soc. 48 (1926) 1207–1219.

- [2] R. Burch, F.A. Lewis, The form of the interaction between palladium and hydrogen, Plat. Met. Rev. 15 (1971) 21–25.
- [3] A. Maeland, T.B. Flanagan, The hydrogen-palladium system, Plat. Met. Rev. 10 (1966) 20.
- [4] G.L. Harris (Ed.), Properties of Silicon Carbide, Published by: INSPEC, the Institution of Electrical Engineers, London, United Kingdom, 1995.
- [5] K.J. Bachmann, H.L. Hwang, C. Schwab (Eds.), Non-stoichiometry in Semiconductors, Elsevier, 2012.
- [6] W.W. Barker, A.F. Wilson, Gross non-stoichiometry and vacancy ordering in the system cerium dioxide-yttrium sesquioxide, J. Inorg. Nucl. Chem. 30 (1968) 1415–1423.
- [7] A. Demont, S. Hébert, J. Höwing, Y. Bréard, D. Pelloquin, Large oxygen nonstoichiometry in La0. 77Sr3. 23Co2. 75C0. 25O8. 40+ δ oxide (δ = 0, 1.3) related to n = 3 RP series, Inorg. Chem. 52 (2013) 1265–1274.
- [8] A.A. Markov, M.V. Patrakeev, V.V. Kharton, Y.V. Pivak, I.A. Leonidov, V.L. Kozhevnikov, Oxygen nonstoichiometry and ionic conductivity of Sr3Fe2-x Sc x 07-δ, Chem. Mater. 19 (2007) 3980–3987.
- [9] L. Nagarajan, R.A. De Souza, D. Samuelis, I. Valov, A. Börger, J. Janek, M. Martin, A chemically driven insulator-metal transition in non-stoichiometric and amorphous gallium oxide, Nat. Mater. 7 (2008) 391.
- [10] V. Simic-Milosevic, N. Nilius, H.P. Rust, H.J. Freund, Local band gap modulations in non-stoichiometric V 2 O 3 films probed by scanning tunneling spectroscopy, Phys. Rev. B 77 (2008) 125112.
- [11] S. Lee, Z.K. Liu, M.H. Kim, C.A. Randall, Influence of nonstoichiometry on ferroelectric phase transition in Ba Ti O 3, J. Appl. Phys. 101 (2007) 054119.
- [12] Y.Y. Lv, B.B. Zhang, X. Li, B. Pang, F. Zhang, D.J. Lin, M. Lu, Dramatically decreased magnetoresistance in non-stoichiometric WTe2 crystals, Sci. Rep. 6 (2016) 26903.
- [13] R. Spinicci, A. Tofanari, A. Delmastro, D. Mazza, S. Ronchetti, Catalytic properties of stoichiometric and non-stoichiometric LaFeO 3 perovskite for total oxidation of methane, Mater. Chem. Phys. 76 (2002) 20–25.
- [14] D. Chen, C. Chen, Z.M. Baiyee, Z. Shao, F. Ciucci, Nonstoichiometric oxides as lowcost and highly-efficient oxygen reduction/evolution catalysts for low-temperature electrochemical devices, Chem. Rev. 115 (2015) 9869–9921.
- [15] M. Gadzira, G. Gnesin, O. Mykhaylyk, O. Andreyev, Synthesis and structural peculiarities of nonstoichiometric β-SiC, Diam. Relat. Mater. 7 (1998) 1466–1470.
- [16] V.A. Izhevskyi, L.A. Genova, J.C. Bressiani, A.H.A. Bressiani, Silicon carbide. Structure, properties and processing, Cerâmica 46 (2000) 4–13.
- [17] A.R. Bunsell, A. Piant, A review of the development of three generations of small diameter silicon carbide fibres, J. Mater. Sci. 41 (2006) 823–839.
- [18] H.Y. Tai, C.T. Lee, L.H. Tsai, Y.H. Lin, Y.H. Pai, C.I. Wu, G.R. Lin, SiC and Si quantum dots co-precipitated Si-rich SiC film with n-and p-type dopants grown by hydrogen-free PECVD, ECS J. Solid State Sci. Technol. 2 (2013) N159–N164.
- [19] C.H. Cheng, C.L. Wu, Y.H. Lin, W.L. Yan, M.H. Shih, J.H. Chang, G.R. Lin, Strong optical nonlinearity of the nonstoichiometric silicon carbide, J. Mater. Chem. C 3 (2015) 10164–10176.
- [20] J. Bullot, M.P. Schmidt, Physics of amorphous silicon-carbon alloys, Phys. Status Solidi (B) 143 (1987) 345-418.
- [21] D.P. Birnie, W.D. Kingery, The limit of non-stoichiometry in silicon carbide, J. Mater. Sci. 25 (1990) 2827–2834.
- [22] H.Y. Tai, Y.C. Chi, C.H. Cheng, P.S. Wang, C.I. Wu, G.R. Lin, Stoichiometry detuned silicon carbide as an orange and white light band solid-state phosphor, RSC Adv. 6 (2016) 7121–7128.
- [23] E. López-Honorato, P.J. Meadows, J. Tan, P. Xiao, Control of stoichiometry, microstructure, and mechanical properties in SiC coatings produced by fluidized bed chemical vapor deposition, J. Mater. Res. 23 (2008) 1785–1796.
- [24] C.T. Lee, L.H. Tsai, Y.H. Lin, G.R. Lin, A chemical vapor deposited silicon rich silicon carbide PN junction based thin-film photovoltaic solar cell, ECS J. Solid State Sci. Technol. 1 (2012) Q144–Q148.
- [25] S.P. Su, C.L. Wu, C.H. Cheng, B.J. Huang, H.Y. Wang, C.T. Tsai, G.R. Lin, Nonstoichiometric SiC bus/ring waveguide based all-optical data format follower and inverter, ACS Photonics 3 (2016) 806–818.

- [26] E. Rauls, J. Elsner, R. Gutierrez, T. Frauenheim, Stoichiometric and non-stoichiometric (1010) and (1120) surfaces in 2H–SiC: a theoretical study, Solid State Commun. 111 (1999) 459–464.
- [27] K.C. Chang, Q. Wahab, L.M. Porter, Observation of a non-stoichiometric layer at the silicon dioxide–silicon carbide interface: effect of oxidation temperature and postoxidation processing conditions, MRS Online Proc. Libr. Arch. 640 (2000).
- [28] S. Wang, S. Dhar, S.R. Wang, A.C. Ahyi, A. Franceschetti, J.R. Williams, S.T. Pantelides, Bonding at the SiC – SiO 2 Interface and the effects of nitrogen and hydrogen, Phys. Rev. Lett. 98 (2007) 026101.
- [29] T. Zheleva, A. Lelis, G. Duscher, F. Liu, I. Levin, M. Das, Transition layers at the Si O 2/ Si C interface, Appl. Phys. Lett. 93 (2008) 022108.
- [30] T.L. Biggerstaff, C.L. Reynolds Jr, T. Zheleva, A. Lelis, D. Habersat, S. Haney, G. Duscher, Relationship between 4 H-Si C/ Si O 2 transition layer thickness and mobility, Appl. Phys. Lett. 95 (2009) 032108.
- [31] X. Shen, M.P. Oxley, Y. Puzyrev, B.R. Tuttle, G. Duscher, S.T. Pantelides, Excess carbon in silicon carbide, J. Appl. Phys. 108 (2010) 123705.
- [32] X. Zhu, H.D. Lee, T. Feng, A.C. Ahyi, D. Mastrogiovanni, A. Wan, L.C. Feldman, Structure and stoichiometry of (0001) 4H–SiC/oxide interface, Appl. Phys. Lett. 97 (2010) 071908.
- [33] J.P. Li, A.J. Steckl, Nucleation and void formation mechanisms in SiC thin film growth on Si by carbonization, J. Electrochem. Soc. 142 (1995) 634–641.
- [34] A. Sagar, C.D. Lee, R.M. Feenstra, C.K. Inoki, T.S. Kuan, Morphology and effects of hydrogen etching of porous SiC, J. Appl. Phys. 92 (2002) 4070–4074.
- [35] D. Sander, W. Wulfhekel, M. Hanbücken, S. Nitsche, J.P. Palmari, F. Dulot, A. Leycuras, Preferential carbon etching by hydrogen inside hexagonal voids of 6H-SiC (0001), Appl. Phys. Lett. 81 (2002) 3570–3572.
- [36] S. Osada, K. Husimi, Y. Fuchi, S. Ohkawa, S. Watanabe, Application of chemical preferential etching on fabrication of epitaxial silicon detectors, Nucl. Instrum. Methods 144 (1977) 353–354.
- [37] M.A. Petrich, K.K. Gleason, J.A. Reimer, Structure and properties of amorphous hydrogenated silicon carbide, Phys. Rev. B 36 (1987) 9722.
- [38] M.M. Rahman, C.Y.W. Yang, G.L. Harris (Eds.). Amorphous and crystalline silicon carbide II: recent developments, in: Proceedings of the 2nd International Conference, Santa Clara, CA. Springer Science & Business Media, 43, 2012.
- [39] Z. Hu, X. Liao, H. Diao, G. Kong, X. Zeng, Y. Xu, Amorphous silicon carbide films prepared by H 2 diluted silane–methane plasma, J. Cryst. Growth 264 (2004) 7–12.
- [40] Y. Matsuda, S.W. King, J. Bielefeld, J. Xu, R.H. Dauskardt, Fracture properties of hydrogenated amorphous silicon carbide thin films, Acta Mater. 60 (2012) 682–691.
- [41] E.P. Guyer, R.H. Dauskardt, Fracture of nanoporous thin-film glasses, Nat. Mater. 3 (2004) 53.
- [42] M.S. Oliver, G. Dubois, M. Sherwood, D.M. Gage, R.H. Dauskardt, Molecular origins of the mechanical behavior of hybrid glasses, Adv. Funct. Mater. 20 (2010) 2884–2892.
- [43] Y. Matsuda, N. Kim, S.W. King, J. Bielefeld, J.F. Stebbins, R.H. Dauskardt, Tunable plasticity in amorphous silicon carbide films, ACS Appl. Mater. Interfaces 5 (2013) 7950–7955.
- [44] M.A. Fraga, R.S. Pessoa, M. Massi, H.S. Maciel, S.G. dos Santos Filho, L.F. Bonetti, L.V. Santos, Synthesis and etching of amorphous silicon carbide thin films with high carbon content, Rev. Bras. Apl. Vácuo 26 (2008) 193–197.
- [45] M. Tello, R. Garcia, J.A. Martín-Gago, N.F. Martínez, M.S. Martín-González, L. Aballe, L. Gregoratti, Bottom-up fabrication of carbon-rich silicon carbide nanowires by manipulation of nanometer-sized ethanol menisci, Adv. Mater. 17 (2005) 1480–1483.
- [46] M. Tabellout, A. Kassiba, S. Tkaczyk, L. Laskowski, J. Swiatek, Dielectric and EPR investigations of stoichiometry and interface effects in silicon carbide nanoparticles, J. Phys.: Condens. Matter 18 (2006) 1143.
- [47] D.V. Savchenko, A. Pöppl, E.N. Kalabukhova, E.F. Venger, M.P. Gadzira, G.G. Gnesin, Intrinsic defects in nonstoichiometric β-SiC nanoparticles studied by pulsed magnetic resonance methods, Sem. Phys. Quan. Elect. Opt. 13 (2010) 43–50.