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Bottom-up Routes to Porous Silicon Carbide

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Abstract. We report on constructive methods providing a large range of high purity porous SiC products. All methods are based on modified sol-gel processes combined with carbothermal reduction. We obtain monodisperse regular pores of well defined diameters by using carbon sphere templates which are removed after SiC infiltration. A different way is a sol-gel based conversion of graphite bodies into SiC, which transfers the porosity from the graphite matrix into the final SiC product. Thus a large variety of porosity features are available, originating either from natural porosity of graphite or from priorly created nano-/ microstructures in the carbonaceous base material. Whereas all our pristine porous sol-gel derived silicon carbide products are semi-insulating, doping is possible, during the growth to modifiy the electrical and optical properties.

Introduction

For sophisticated applications porous SiC is usually fabricated destructive by labour intensive electrochemical etching of electronic quality SiC wafers. Although notable progress has been achieved in the recent past [1], high quality porous structures as needed for photonic applications with silicon carbide have not been achieved so far. However, it depends on the intended application, which kind of porosity is sufficient. There are other constructive fabrication paths, using SiC powder, various binders and pressure to achieve ceramic porous SiC. However, they are inappropriate for electronic or photonic applications.

We report here on rather inexpensive constructive processing methods providing a large range of products of high purity porous SiC. All methods to be presented are based on a sol-gel process combined with carbothermal reduction. Thereby we obtain efficient polycrystalline 3C-SiC growth at around 1800°C. In this way porous SiC can be grown on various substrates like commercial SiC wavers or sapphire and as free standing bulk material. Fig. 1 shows an example of a free-standing porous 3C-SiC sample grown directly via our sol-gel supported process, which allows also cost-efficient fabrication in large dimensions (cm^3). This offers applications not only in electronics and photonics but as well e.g. for filtering, catalyst support or sensor applications in harsh environment providing particularly large surface areas [2].

Experimental and Discussion

Approach I

The starting material is a sucrose containing silica sol, which was prepared via hydrolysis and condensation of tetraethoxysilane (TEOS) in ethanolic solution with deionized water in the presence of hydrochloric acid. A specific amount of sucrose, leading to a Si:C ratio of 1:4 was added via prior dissolution in deionized water. The obtained sol is either used immediately (coating, infiltration) or is kept for further processing. A whole range of other saccharides can be used alternatively. In our case, sucrose was chosen due to its good processability and very well studied degradation behaviour.

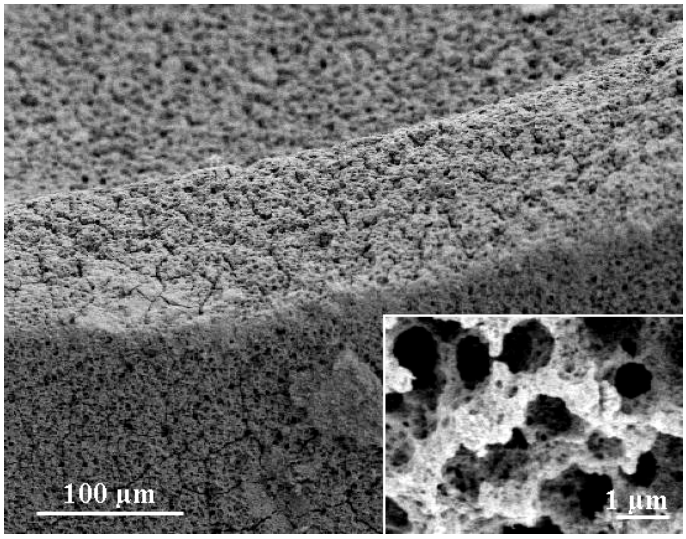

Fig. 1: Macroporous sol-gel 3C-SiC. There are no regular pores. The sample size can be cm^3.

Approach II

Pre-structured SiC with well defined monodisperse periodically arranged pores is achieved by using a close packed two or three dimensional carbon spheres template [3, 4]. This regular structure is infiltrated by filling the voids between the spheres with the above described SiC precursor solution. After an oxygen free high temperature annealing step, which converts the precursor into SiC, the spherical templates are removed. This is either done by baking the obtained composite structure at 1000˚C in air for short time or by etching in an oxidizing agent, e.g. hydrogen peroxide (H_2O_2), leaving a silicon carbide scaffold consisting of uniform spherical interconnected pores (see fig. 2). Therein the final pore size can be adjusted by the initial diameter of carbon spheres used for the template. The carbon particles therefore can be specifically synthesized with a size between 100nm and 2µm and the template thereof is grown by common colloidal self-assembly techniques. The material morphology of the finally obtained SiC depends amongst other parameters especially on the film thickness. Thin layers up to 20 microns can be obtained completely monocrystalline (3C-SiC) with an embedded structure of well ordered hollow spheres. Thicker films are usually polycrystalline, consisting of interconnected microcrystals surrounding hollow spheres.

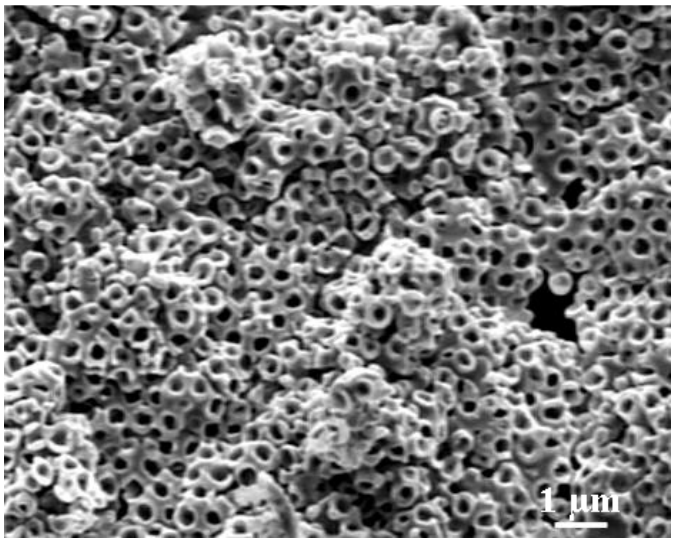

Fig. 2: Monodisperse uniform pores achieved after infiltration of a regular carbon spheres colloidal crystal with sol-gel SiC. After removing of the carbon template well defined porous SiC is left.

Approach III

Using another modified sol-gel supported process we have been able to convert any graphite part into 3C-SiC [5]. With this technique carbon bodies (e.g. from graphite or glassy carbon) can either be completely or superficially converted into porous silicon carbide without deformation or shrinkage. Unlike the first method, this one utilises the gaseous by-products, created during high temperature decomposition of the granulated sol-gel based SiC-precursor material. Thereby two each other accompanying processes take place. Carbon monoxide (CO) increases porosity of the carbonaceous material due to oxidation. On the other hand, the interaction of gaseous silicon monoxide (SiO) with carbon generates first silicon carbide seed crystals within the pores of the carbon material. Silicon carbide vapour, created along with CO and SiO gas, condensates on these SiC seeds, causing crystal growth inside the structure, finally covering or even completely filling the pores. While both of these processes continue until the precursor is used up, the carbon body is transformed to SiC from the outside towards the center of the sample. This has been investigated in detail by stopping the conversion process at certain stages. The porosity of the obtained SiC body depends mainly on the initial porosity of the previous carbon body. The main advantage of this method is the presservation of shape and size of a given graphite body after conversation into silicon carbide. Thus, any porous structure either 'natural' or easily artificially prepared in the graphite raw material will be converted into SiC. Figures 3 and 4 give two examples of such converted graphite.

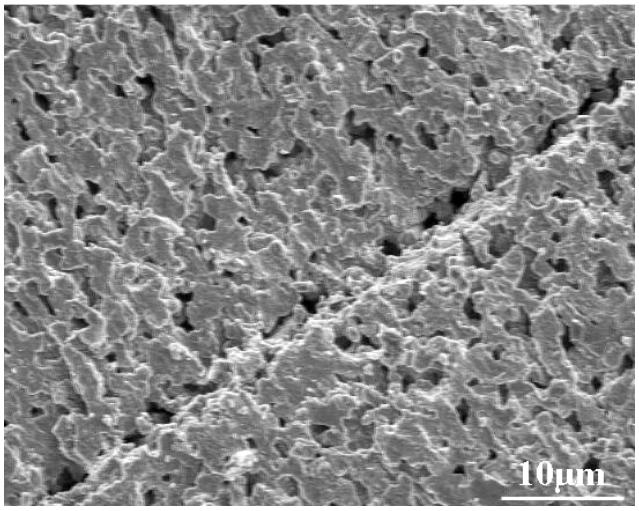

Fig. 3: SEM image of the cross section of a converted graphite sample with micron sized pores.

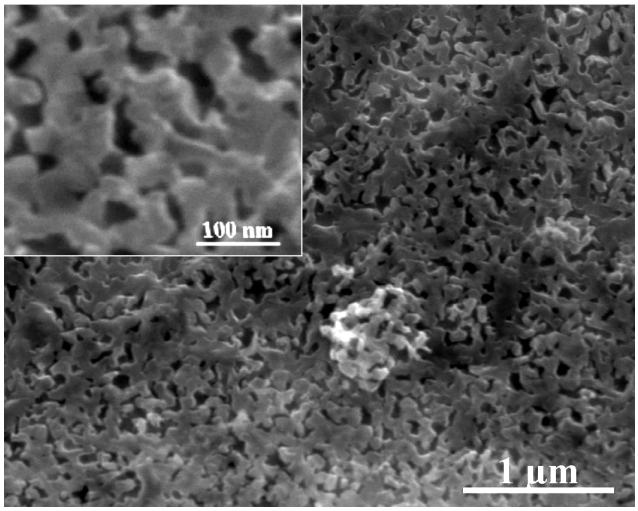

Fig. 4: SEM image of the cross section of a converted graphite sample with nanometer sized pores.

The materials have been verified as 3C-SiC by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The pore size and morphology of the porous samples have been determined by scanning electron microscopy (SEM).

Doping

Unlike customary SiC, sol-gel based SiC does not contain any unwanted contamination such as the unavoidable nitrogen donor in customary SiC. Thus the sol-gel SiC is semi-insulating and needs further doping if necessary for electronic or optical applications. As probing dopants, we have used phosphorous, nitrogen, boron and aluminium, which are the technologically most requested ones concerning 'conventional' semiconductor SiC and are well known from different characterization methods. In contrast to commercially available SiC, with our method p-type doping and semi-insulating properties are possible without nitrogen donor compensation or activation of intrinsic defects,

respectively. In all above mentioned procedures foreign ions can be introduced in two different ways. The dopant can be added during SiC precursor preparation, by adding either itself or a soluble compound to the initial solution. Suitable candidates are nitrates (N doping), borates (B), phosphates (P) or chlorides (e.g. for Al). During degradation of the precursor, during annealing at 1800°C, the foreign ions are automatically built-in into the growing SiC crystal structure.

The other more difficult way is providing the dopant via gas phase during the high temperature annealing process (e.g. nitrogen). This method is only suitable for selected elements. However, also other doping elements are possible, but not yet tested. In order to proof successful incorporation of dopants we used electron paramagnetic resonance (see for example figure 5) and optical spectroscopy.

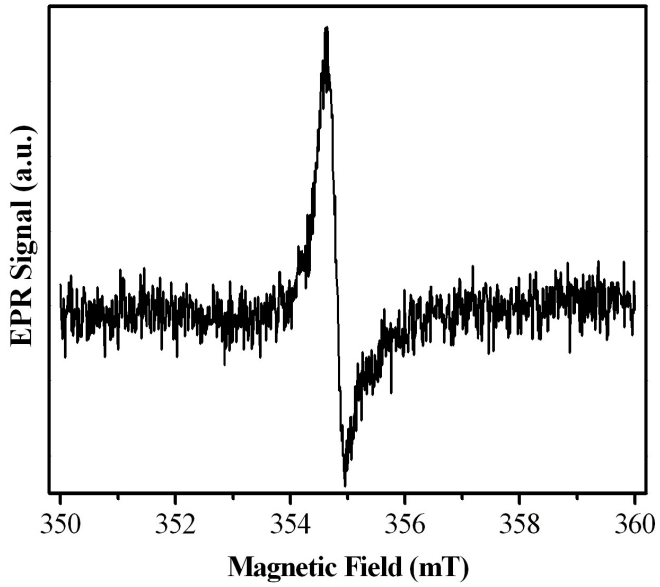

Fig. 5: EPR spectrum of a free gas phase grown SiC converted porous sample doped with nitrogen, introduced by adding nitric acid to the initial precursor solution. Observed is a so-called powder spectrum of the nitrogen donor known from crystalline 3C-SiC with g = 2.0050 (T = 11K, x-band). The characteristic ^{14}N hyperfine interaction with 3.5MHz is not resolved in the powder spectrum. The donor concentration can be determined to be $10^{12}cm^{-3}$.

Conclusions

The presented sol-gel based growth processes deliver very clean materials of selectable pore size and arrangements for porous SiC. Such material is suitable for photonic as well as for electronic applications. The conversion of carbonaceous bodies into porous lightweight and stable silicon carbide, offers a useful easy method for the production of requested SiC parts, without having to process the hard SiC directly. Two different doping procedures allow n- and p-type doping with shallow donors and shallow acceptors. The described preparation methods allow the easy and cost efficient production of pure clean porous SiC, they as well adequate for fabrication amounts and sizes exceeding the laboratory scale.

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