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Silicon Carbide Formation in Reactive Silicon-Carbon Multilayers

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Abstract. An alternative low thermal budget silicon carbide syntheses route is presented. The method is based on self-propagating high-temperature synthesis of binary silicon-carbon-based reactive multilayers. With this technique, it is possible to obtain cubic polycrystalline silicon carbide at relatively low annealing temperatures by a solid state reaction. The reaction starts above 600 °C. The transformation process proceeds in a four-step process. The reaction enthalpy was determined to be (-70 ± 4) kJ/mol.

Introduction

A large variety of growth and formation techniques for cubic silicon carbide films have been proposed and evaluated, for example, sublimation growth [1], liquid phase epitaxy [2], chemical vapor deposition [3], molecular beam epitaxy (MBE) [4], magnetron sputtering [5], ion beam synthesis [6] and self-propagating high-temperature synthesis of powder mixtures [7-9]. For different applications, low cost and low thermal budget techniques are desirable, especially in the field of microelectromechanical systems and coating applications. Beside the thin film technologies an alternative route of forming SiC is the application of self-propagating reactions (SPR) via annealing of silicon and carbon powder mixtures as demonstrated in [7-9]. In these studies it has been shown that different SiC polytypes can be formed in dependence on the C source used for the SPR. For the application of SPR for thin film technologies, the powder mixture has to be transformed into a multilayer system consisting of Si-C bilayers stacked into a layer with a certain total thickness on a substrate of choice.

This goal can be achieved by combining the widely used magnetron sputtering techniques with the rapid thermal processing technology (RTP). In this contribution, the direct synthesis of SiC on Si or on SiO_2/Si substrates in a binary Si-C multilayer system deposited by magnetron sputtering and subsequently annealed using RTP is reported. The phase formation and structural evolution was studied in dependence on the annealing temperature. A special emphasis was given to the reaction enthalpy in the Si-C multilayer system.

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Experimental

The samples were prepared by magnetron sputtering using high purity silicon and carbon targets. Alternating layers of Si and C, with layer thickness of 50 nm each and a bilayer periodicity λ of 100 nm, are repeatedly deposited at room temperature onto the substrates until an overall film thickness of 1 µm is achieved. Two types of substrates were used for the deposition: (1) boron doped p-type Si(100) with a specific resistance of 5 mΩ cm and (2) the same substrate as in (1) but covered with a 90 nm thick SiO_2 layer grown by dry oxidation. The samples were annealed in a RTP furnace in pure Ar atmosphere and in a temperature range between 500 and 1100°C with annealing times of 1 and 5 min. The heating-up rate was set to 10 K/s. The cooling-down rate was kept at 4 K/s. The morphology of the samples was studied with scanning electron microscopy (SEM). The structural investigations were performed by X-ray diffraction (XRD) and reflection Fourier transform infrared (FTIR) measurements. Differential scanning calorimetric (DSC) and differential thermal analysis (DTA) measurements were performed to investigate the phase formation and determine reaction enthalpy.

Results and Discussion

Fig. 1 shows cross section and plane view SEM images of the as deposited reactive multilayer film deposited on bare silicon substrate. The dark grey layers in Fig. 1 (a) correspond to C whereas the light grey layers stem from Si in the multilayer stack. The interface between Si and C shows a wave like behaviour. This is reflected in the plane view image as given in Fig. 1 (b), where a grain like structure of the upper silicon film is evident. The measured average thickness of the Si and the C layers are 53 and 48 nm, respectively

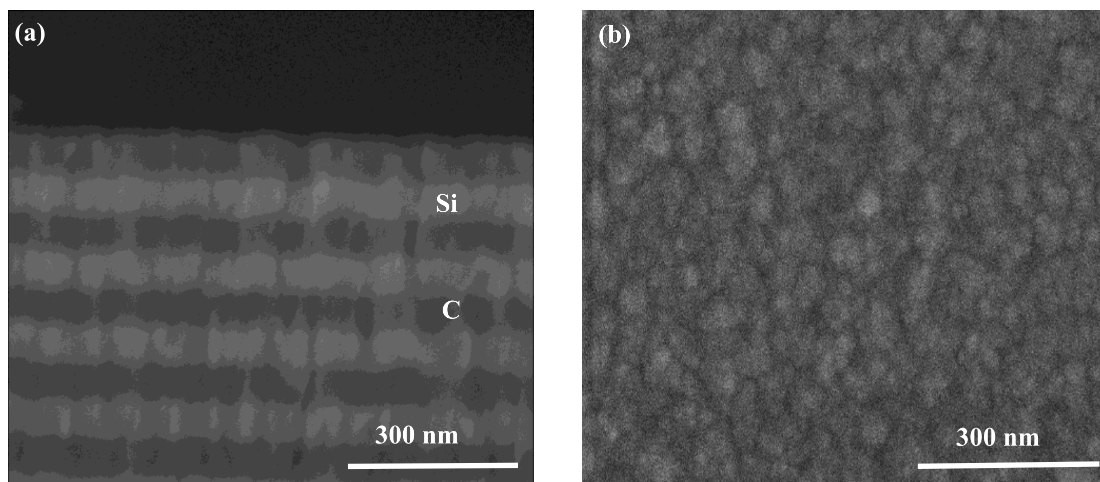

Fig. 1. SEM images of the as deposited silicon-carbon reactive multilayer stack: (a) cross section of the near surface region, (b) plane view of the surface.

Fig. 2 shows a measured characteristic set of grazing incidence XRD patterns of the RTP annealed samples in comparison to the as-deposited sample. The XRD patterns were measured at an incidence angle of 7°. The patterns can be divided into two groups. The first group combines the spectra of the deposited sample and the samples annealed below 700°C. The second group consists of all samples annealed at 700°C and above. The characteristic feature of the first group is the appearance of three broad diffraction peaks suited approximately at 28°, 34° and 57°. The peak at the lowest angular position can be assigned to Si(111). Such peak location and peak form is typical for amorphous or nanocrystalline (nc) Si structures. Furthermore, reflections that could be assigned to crystalline C of any nature are completely absent, indicating that the C is initially amorphous. A similar spectra was obtained from Si/C/Si triple layers in [10]. The peak at 34° is located in the region of the α-SiC(100) and the β-SiC(111) peaks stemming from nc-SiC crystallites formed at the interfaces of the Si-C layers. The peak at around 57° can be interpreted as the alloying of Si with C during the deposition

of the Si-C bilayers. The Scherrer analysis revealed crystallite size values between 2.0 and 2.5 nm for Si and SiC, respectively. The second group of XRD spectra is characterized by a distinct crystallization of the Si layers in the multilayer stack evidenced by the reduction of the full width of the half maximum of the Si(111), Si(220) Si(311) and Si(331) peaks and the increase of their intensity. With increasing annealing temperature the very broad peak located at 34° splits into two broad peaks.

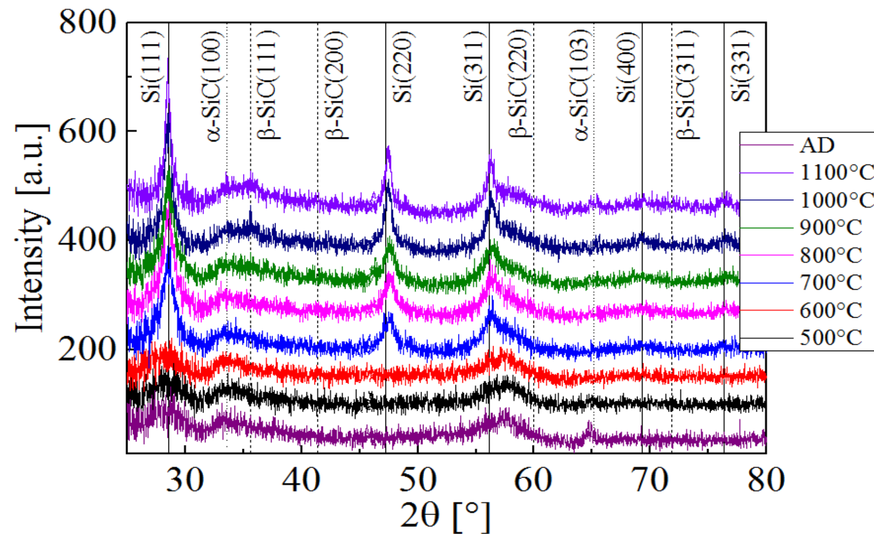

Fig. 2 Compiled grazing incidence XRD patterns from as deposited and annealed Si/C bilayer stacks deposited on Si(100) without SiO_2. RTP annealing for 1 min. The spectra are shifted along the vertical direction.

They can be assigned to nc-α-SiC(100) and the nc-β-SiC(111). This can be caused either by a mixture of α-SiC and β-SiC, or β-SiC and β-SiC containing stacking faults with a hexagonal structure. The broad peak located at approximately 57° with a symmetric peak form for the as deposited state and for the samples annealed at temperatures below 700°C transforms into a peak with an asymmetric peak form. The sharp part of the diffraction peak is located at the lower angular position and stems from Si(311). The broad shoulder at the higher angular position of this peak can be related to a combination of two overlapping peaks; the Si(311) peak of the C alloyed Si and the β-SiC(220) peak. The XRD pattern of the samples annealed at 5 min are qualitative similar. For both annealing times the temperature dependent structural evolution was independent on the substrate, indicating weak dependence of the reaction and structure formation on the substrate and an imprinting of the transformation process by layer deposition and annealing conditions.

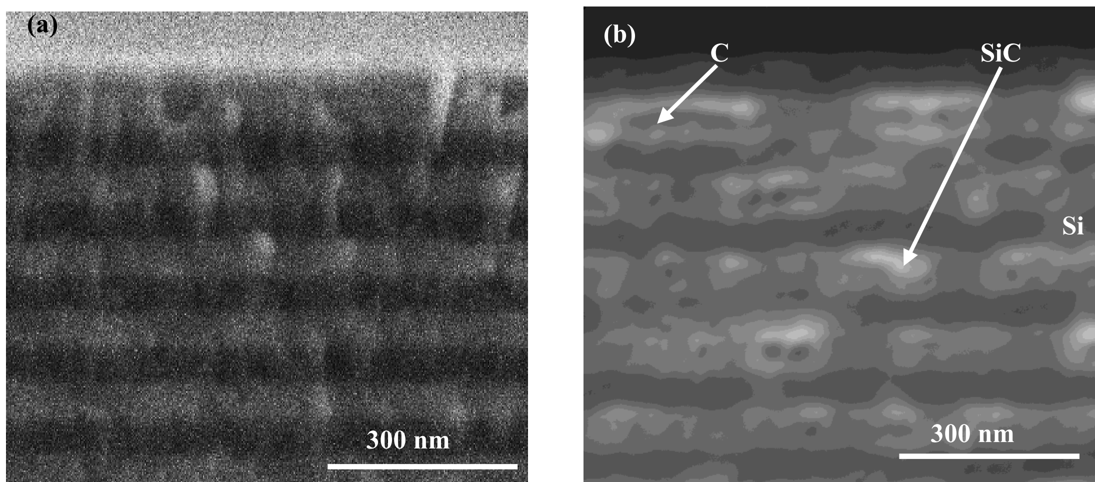

Fig. 3 Cross section SEM images of the silicon-carbon reactive multilayer stack RTP annealed at 500°C and 1100°C for 5 min.

Fig. 3 shows cross section images of the Si-C reactive multilayer stack annealed at 500°C (Fig. 3 (a)) and 1100°C (Fig. 3 (b)) for 5 min. The measured average Si and C layer thicknesses for the 500°C sample were 48 and 45 nm, respectively. The reduced layer thicknesses stem from the compaction of the sputter deposited material. The contrast and the morphology of the interfaces in Fig. 3 (a) is very similar to the non-annealed state as shown in Fig. 1 (a) indicative for a missing or very weak SiC formation. Conducted FTIR reflection studies have not shown the evidence of a SiC phonon vibration frequencies. In case of annealing at 1100°C, the morphology of the layers is changed. The Si layers are enlarging up to 80 to 90 nm at the expense of the dark grey carbon layers. In the centre of the Si layers, the contrast remains which indicates a non-consumed Si. The contrast of the thickened part of the Si layer is slightly different indicating that SiC has been formed. At different locations, a coalescence of the layers with the Si contrast appears. Nevertheless, some dark grey areas are remaining. Therefore, the C layer is not fully transformed. The morphology change points out that the SiC formation occurs mainly in the C layer by Si diffusion into C rather than by C diffusion into Si. Infrared measurements revealed a reflection peak at 799 cm^{-1} which can be assigned to the β-SiC TO vibration frequency. This phonon mode position is characteristic for compressive strained SiC. A second weaker peak was found at 603 cm^{-1} characteristic for a $Si_{1-x}C_x$ alloy formation [11]. The Si grain size increases up to 10 nm for the highest annealing temperature. For SiC up to 6 nm was obtained.

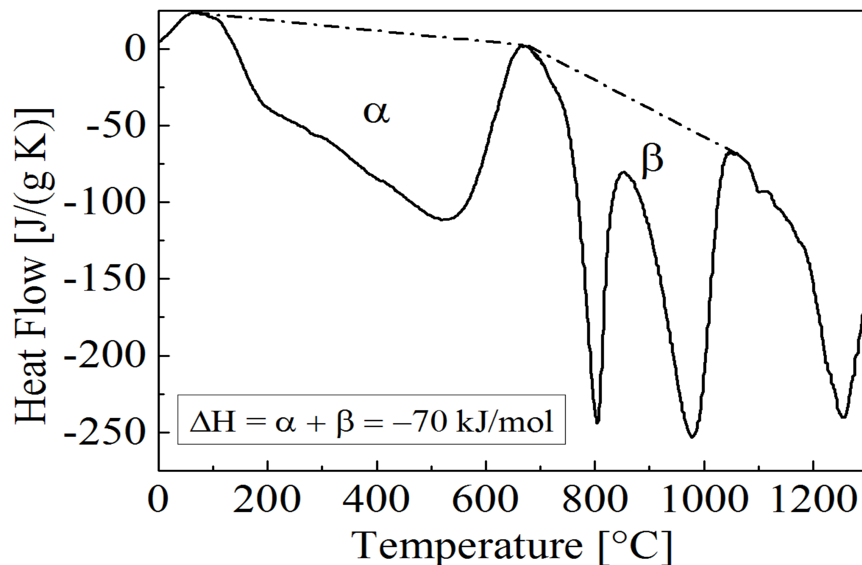

Fig. 4 Combined heat flow thermogram measured with DSC and DTA of the Si-C multilayer annealed with a heating rate of 20 K/min.

Fig. 4 depicts the combined thermal analysis. The broad DSC α peak between 110°C and 700°C shows a shoulder peak at around 200°C and a maximum between 520 and 530°C. This peak might be attributed to the gradual crystallization process of the deposited Si layers and C layers. The crystallisation process causes densification of the Si and C layers evidenced by the SEM investigations shown in Figs. 1 and 3. The second process contributing to this structure is the Si and C interdiffusion at Si-C interface regions in the multilayer supported by the shift of the Si(311) XRD peak for annealing temperatures below 700°C (see Fig. 2). The subsequent decomposition of the alloy leads to nucleation of SiC at the interface. The nucleation of SiC by reaction of Si with elemental C occurs even below 500°C [12]. The two exothermic peaks β at 803°C and 980°C are related to intense SiC phase formation and growth. The double peak structure might stem from two different growth mechanisms. At lower temperatures columnar growth occurs, whereas at higher temperature three dimensional growth dominates as observed for MBE growth [4]. A schematic model of the transformation process can be found in [10]. The determined total reaction enthalpy was (-70±4) kJ/mol in agreement with literature values on powder being in the range of -69 to -73 kJ/mol [8, 9].

Summary

The imprinted transformation process in Si-C multilayer stacks is a multistep process and consist of four steps: (1) layer densification, (2) Si and C interdiffusion, (3) SiC nucleation and (4) SiC growth with temperature dependent growth modes. The SiC growth starts between 600 and 700°C and results in a compressively stressed polycrystalline α- and β-SiC. The reaction enthalpy was determined to be -70 kJ/mol.

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