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Growth controlling of diamond and β-SiC microcrystals in the diamond/β-SiC composite films

Hao Zhuang, Xin Jiang *

Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany

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ABSTRACT

Diamond/β-SiC composite films are prepared with varied gas phase compositions at increased microwave power density in the microwave plasma chemical vapor deposition process. Scanning electron microscope (SEM), X-ray diffraction (XRD) and micro-Raman measurements are carried out to characterize the change of phase composition, morphology and orientation of the composite films. A reduction in the growth rates of the diamond and β-SiC microcrystals is observed which results in the higher density of defects in the diamond crystals and lower growth rates of the composite films in comparison with those of the pure diamond film. XRD measurements show that the addition of a low CH_4 flow rate can lead to the (100) oriented growth of the β-SiC phase, while an increase in the CH_4 flow rate results in a randomly oriented β-SiC phase in the composite film. Based on the overall experimental observation, the growth mechanism of the composite films at increased microwave power density is proposed. The continuous formation of defects on the diamond and β-SiC crystals (induced by the bonding of Si and excess carbon containing species onto diamond and β-SiC crystals, respectively) and their subsequent etching by atomic hydrogen are important in affecting the growth rates and orientation of the composite films.

1. Introduction

Diamond and β-SiC are both well-known for their excellent physical and chemical properties which make them promising for mechanical and electronic device applications [1–3]. Driven by the ambition to create a superior material with combined advantages of diamond and β-SiC, the fabrication of diamond/β-SiC composite films was firstly launched in 1992 using the chemical vapor deposition technique [4]. The co-growth of diamond and β-SiC phases is achieved by the introduction of a small amount of tetramethylsilane ($Si(CH_3)_4$, TMS) into the gas phase while keeping the other parameters similar to the diamond deposition. During the course of time, this new film system becomes a promising candidate in various applications, ranging from improving the adhesion of diamond on different technologically important substrates [5,6] to serving as platforms for sensor applications [7]. Especially in the area of biosensor, the good chemical stability, good biocompatibility and possibility in the surface functionalization of diamond and β-SiC make this composite material a very promising candidate. Moreover, the successful achievement in controlling the wettability of the surface of the composite films even broadens their applications in studying the protein–surface interaction, driving flow in microfluidic devices, increasing heating transfer efficiencies in heating/cooling systems, etc. [7]. Nevertheless, the key to unlock its full potential is the ability to control its growth to obtain specific structures with desired properties. A deep understanding in the growth mechanism of the composite film is thus a prerequisite in achieving this goal, which forms the aim of our years of dedicated research. For a long time, only nanocrystalline diamond/β-SiC films have been synthesized due to the disturbed growth of both diamond and β-SiC crystals [5,6,8–13]. This is because: even though the TMS content is low in comparison with CH_4 (TMS/CH_4 = 1%–8%), it induces a high secondary nucleation rate on the diamond crystals and inhibits their homoepitaxial growth [4,8]. On the other hand, the much higher CH_4 concentration renders a carbon rich atmosphere for the β-SiC growth, leading to its poor crystallinity, too. This situation has not been changed until recently, when an increased microwave power density has been applied for the deposition of composite films [14]. It leads to a significant increase in the concentration of atomic hydrogen ([H]) in the plasma. Through an effective etching process, the high [H] improves the selectivity of the bonding of silicon and carbon containing species onto the β-SiC and diamond crystals, respectively (named as "hydrogen induced selective growth model"), resulting in the growth of microcrystalline high quality composite films [14]. Nevertheless, more detailed studies are still required to fully understand the growth mechanism of the composite films at this increased microwave power density. In this paper, we will focus on the investigation of the influence of different gas phase compositions

* Corresponding author. Tel.: +49 271 7402966; fax: +49 271 740 2442.
E-mail address: xin.jiang@uni-siegen.de (X. Jiang).

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on the growth of the composite films at increased microwave power density. Reduced growth rates of diamond and β-SiC microcrystals have been observed which drastically affect the growth rate and the orientation of the composite films.

2. Materials and methods

Mirror polished single-crystalline p-type Si (100) wafers were used as substrates for the deposition of microcrystalline diamond/β-SiC composite thin films. The Si wafers were pretreated by the nanodiamond particles in order to achieve a high diamond nucleation density ($>10^{11}/cm^2$). The substrate was placed on a Mo holder with a diameter of 52 mm which is located on a water cooled substrate table. A MWCVD reactor equipped with a 5 kW generator was employed for the growth of the composite film. The reactive gas features a mixture of H_2, CH_4 and TMS (1.15% diluted in H_2). For all of the depositions, the MWPD is fixed at 30 W/cm^3 (calculated according to Reference [15]) and the substrate temperature is maintained at ~800 °C which is measured by an optical pyrometer. Different CH_4 flow rates (0–7 sccm) and TMS flow rates (0–15 sccm) are employed to investigate the influence of the gas phase composition on the growth of the composite films and the total flow rate is kept at 400 sccm. Except for the microwave plasma, no external heating source was applied to the substrate. The deposition was carried out for a total time of 6 h for pure β-SiC films and 8 h for diamond and composite films. A scanning electron microscope (SEM, Zeiss Ultra 55) was used to obtain the plane and cross-sectional microstructures of the samples. To determine the phase composition and orientation of the samples as well as their variation with different deposition conditions, X-ray diffraction (XRD) measurements are performed in the 2θ range of 30–100° with a step size of 0.05°. Micro Raman scattering studies are carried out to understand the structural order and phase purity of both diamond and β-SiC crystallites, as well as the presence of non-diamond phases in the composite films based on the typical phonon lines in the obtained spectra. The 532 nm line of a Nd:YVO_4 diode-pumped solid-state laser was used as the excitation source.

3. Results and discussion

Before directly starting the investigation of the growth of composite films, the deposition of pure diamond and pure β-SiC thin films was carried out first to understand their growth behavior, i.e. growth rate, crystal size and orientation, under the above deposition conditions. Fig. 1(a) shows the SEM surface and cross-sectional images of the pure diamond film deposited by employing only 5.5 sccm of CH_4. It can be observed that the polycrystalline diamond film with good crystallinity has been obtained. The cross-sectional image shows the columnar growth nature of diamond and its growth rate is determined to be ~180 nm/h by measuring the thickness of the film. Such growth behavior agrees well with the literature [16]. Fig. 1(b) and (c) presents the SEM images of the pure β-SiC films deposited under different TMS flow rates. It is clearly observable that, the reduction of the TMS flow rates from 10 to 5 sccm leads to a drastic decrease in the growth rate of the β-SiC film from ~100 nm/h (Fig. 1(b)) to ~50 nm/h (Fig. 1(c)). Nevertheless, regardless of the great differences in the concentrations of TMS (hundreds of ppm) and CH_4 (1.4%) during deposition, the growth rate of the β-SiC films is still comparable with that of the diamond film. This is due to the more efficient production of SiH_3 sources with excellent rigidity in sp^3 hybridization through the H abstraction process in the plasma [11] and forms the basis of our co-deposition of diamond and β-SiC phases in the MWCVD process. In addition to the different growth rates, a change in the surface morphology and orientation of the β-SiC films can be also observed while varying TMS flow rates. At a TMS flow rate of 10 sccm, a randomly oriented polycrystalline β-SiC film has been obtained with a crystal size of ~0.5 μm, which is smaller than that of the pure diamond film (~2 μm). A reduction of the TMS flow rate to 5 sccm leads to the formation of textured β-SiC crystals. This is due to the hetero-epitaxial growth of β-SiC on the Si substrate (as supported by the XRD patterns in Fig. 1(d)) and has been discussed in detail in one of our previous publications [17].

After understanding the growth behavior of pure diamond and pure β-SiC thin films, the investigation of the influence of different TMS flow rates on the growth of the composite films was firstly carried out. The films were deposited with different TMS flow rates ranging from 5 to

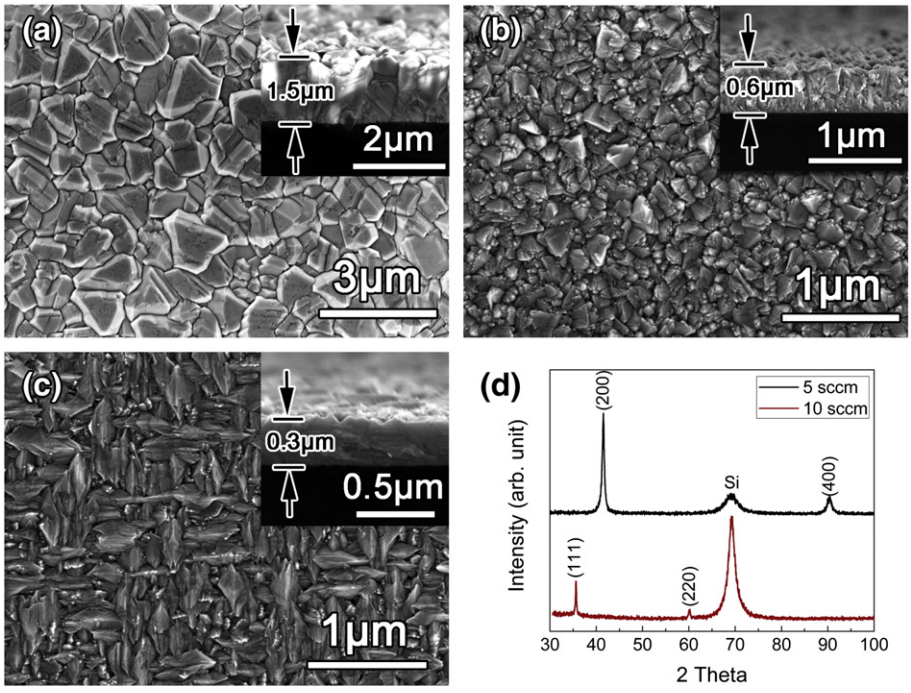

Fig. 1. (a–c) SEM surface and cross-sectional images of the pure diamond and pure β-SiC films: (a) pure diamond film deposited at $CH_4 = 5.5$ sccm, growth time = 8 h; (b) pure β-SiC film deposited at TMS = 10 sccm, growth time = 6 h; (c) pure β-SiC film deposited at TMS = 5 sccm, growth time = 6 h. (d) XRD patterns of the β-SiC films shown in (b) and (c).