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Formation of silicon carbide at low temperatures by chemical transport of silicon induced by atmospheric pressure H_2/CH_4 plasma

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Abstract

Using atmospheric pressure, very high-frequency (VHF) plasma, silicon carbide (SiC) films were formed on single-crystal Si(001) substrates from a hydrogen (H_2) and methane (CH_4) mixture. The H_2/CH_4 plasma etched the cooled surface of a Si-coated electrode, generating SiH_n species, and transported them to the heated substrate surface with interactions with CH_n species generated from the decomposition of CH_4 molecules. By virtue of the carbonization of the substrate surface in the beginning of deposition, a (001)-oriented 3C–SiC film could be formed at a substrate temperature (T_{sub}) as low as 300°C, although the film-forming reaction was more enhanced at the higher T_{sub} due to the smaller etching rate of the growing SiC film by atomic hydrogen. At T_{sub} = 130°C, however, the full crystallization of the film did not occur, resulting in the deposition of a polycrystalline 3C–SiC film with the poorer crystallinity. The optical emission spectra of the plasma revealed that the Si substrate was etched by atomic hydrogen in addition to the Si-coated electrode at 130°C.

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1. Introduction

Silicon carbide (SiC) is a promising wide band gap semiconductor material, which is suitable as a high-tech material for high-frequency, high-power and high-temperature electronic devices as well as for mechanical applications [1–6]. There exist more than 200 different SiC polytypes, which all differ in the stacking sequence of the Si/C double layers [7]. Among the polytypes, hexagonal ones (4H and 6H) and cubic one (3C) are of major technical interest. In the case of homoepitaxial growth of 4H– or 6H–SiC films, the size limitation of SiC wafers may restrict the development of SiC devices. Since 3C–SiC is also the desirable material for device application, the heteroepitaxial growth of 3C–SiC on Si substrates is one of the best solutions for supplying large SiC substrates [8,9]. 3C–SiC is also of great interest because of its possible application to the substrate material for the epitaxial growth of gallium nitride (GaN), the material for the light emitting diodes and laser diodes in the violet and blue light regions [10].

For the preparation of crystalline 3C–SiC films, low-pressure chemical vapor deposition (LPCVD) and reactive magnetron sputtering are generally used [8,9,11,12]. In these techniques, the substrate temperature must exceed 1000°C, if high quality films are desired. However, high temperatures are often detrimental to the substrate materials. Thus, it is necessary to find the suitable deposition procedures, which can be held as low substrate temperatures as possible.

For the low-temperature and high-rate growths of functional thin films, we have developed an atmospheric pressure plasma CVD (AP–PCVD) technique [13]. In the AP–PCVD process, stable glow plasma excited at atmospheric pressure by a 150-MHz very high frequency (VHF) power has been effectively used to deposit thin films. In our previous reports, we studied AP–PCVD of SiC on Si substrates using silane (SiH_4) and methane (CH_4) dual sources [14–16] or monomethylsilane (CH_3SiH_3) single source [16] diluted with helium (He) and hydrogen (H_2). It was shown that 3C–SiC films, having polycrystalline columnar structure, could be grown at a

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substrate temperature of 800°C with high deposition rates greater than 3nm/s, which is far larger than those obtained by LPCVD [17–19]. Note that increasing concentration ratio of H_2 to the source gases is primarily important not only to increase the amount of highly dissociated silane radicals (Si and SiH), which react with CH_n (n = 2–4) species and form deposition precursors preserving Si–C bonds in the plasma, but also to increase the order of the crystalline structure by suppressing the random generation of crystalline nuclei at the surface [16]. Therefore, we have considered that the heteroepitaxial growth of 3C–SiC is possible when the structure of the initial growth layer is improved.

The present study deals with the formation of 3C–SiC films on Si substrates by chemical transport of Si induced by atmospheric pressure H_2/CH_4 plasma. According to the temperature dependence of etching rate of Si by atomic hydrogen, SiH_n species are mainly generated at the cooled surface of a Si-coated electrode and transported to the heated substrate surface [20]. Thus, SiC films can be formed only by using H_2 and CH_4 mixtures. Note that the atmospheric pressure H_2/CH_4 plasma is considered to carbonize the substrate surface and transform Si into 3C–SiC in the beginning of deposition, which is profitable for the heteroepitaxial growth of 3C–SiC films on Si substrates [21,22]. In this paper, we present some results on the structural characterizations of the deposited SiC films and discuss the deposition process. Furthermore, we analyzed the atmospheric pressure H_2/CH_4 plasma by optical emission spectroscopy (OES) measurements.

2. Experimental details

The experiments were conducted in the AP–PCVD system used in our previous studies [14–16]. Fig. 1 shows the schematic illustration of the experimental setup. The AP–PCVD system had a cylindrical rotary electrode with a diameter of 300mm and a width of 100mm. By rotating electrode, the source gas molecules in the chamber could be carried by a high-speed viscous flow and homogeneously introduced into the narrow gap region between the electrode and a substrate. The substrate was vacuum-chucked on the substrate heating stage made of SiC-coated graphite. By supplying 150MHz VHF power, atmospheric pressure plasma was generated and confined in the gap region as shown in Fig. 1.

Table 1
Experimental conditions

Parameter	Condition
Carrier gas	He
CH_4 concentration (%)	0.25
H_2 concentration (%)	99.75
Process pressure (Pa)	1×10^5
VHF power (W)	1000
Plasma gap (mm)	0.5
Electrode rotation speed (rev./min)	1000
Substrate temperature (°C)	130–800

The experimental conditions are listed in Table 1. Prior to a series of experiments, the electrode surface was coated with Si using He/SiH_4 plasma. Single-crystal Si(001) wafers with a resistivity of 10–20Ω cm were used as substrates. The wafers, cut into a size of $10\times90mm^2$, were cleaned by the room temperature wet cleaning process [23]. Before each experiment, the chamber was exhausted to a pressure less than 10^{-6}Torr and then filled with the process gas mixture to a pressure of 760Torr. SiC films were deposited without substrate scanning; then the films were formed in a rectangular region defined by the width of plasma (10mm), which was determined by the width of substrate, and the plasma length (approximately 40mm). During deposition, the gas composition and the process pressure were maintained constant, and optimized values were employed for the plasma gap and the electrode rotation speed under supplying a sufficiently large VHF power of 1000W. The substrate temperature (T_{sub}) was varied as a parameter. Since most part of the electrode surface is cooled by the process gas in the chamber, the temperature of the electrode surface did not rise over 60°C even when the substrate was heated up to 800°C.

The structure and crystallinity of the SiC films were evaluated at the central portion of the deposited area by infrared (IR) absorption spectroscopy and reflection high-energy electron diffraction (RHEED). The IR absorption spectra were measured by a Fourier transform IR spectrometer (Shimadzu FTIR-8600PC) in the wavenumber range of 400–3500cm^{-1}. The RHEED observations were conducted in a transmission

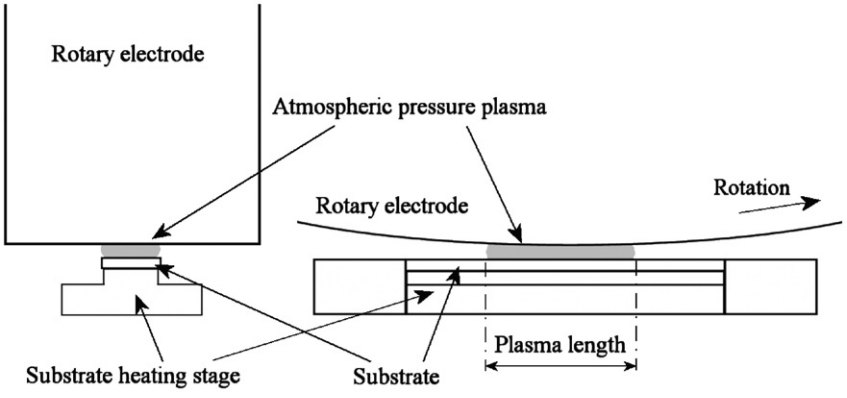

Fig. 1. Schematic illustration of the experimental setup.