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Growth of boron doped hydrogenated nanocrystalline cubic silicon carbide (3C-SiC) films by Hot Wire-CVD



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ABSTRACT

Boron doped nanocrystalline cubic silicon carbide (3C-SiC) films have been prepared by HW-CVD using silane (SiH₄)/methane (CH₄)/diborane (B₂H₆) gas mixture. The influence of boron doping on structural, optical, morphological and electrical properties have been investigated. The formation of 3C-SiC films have been confirmed by low angle XRD, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infra-red (FTIR) spectroscopy and high resolution-transmission electron microscopy (HR-TEM) analysis whereas effective boron doping in nc-3C-SiC have been confirmed by conductivity, charge carrier activation energy, and Hall measurements. Raman spectroscopy and HR-TEM analysis revealed that introduction of boron into the SiC matrix retards the crystallanity in the film structure. The field emission scanning electron microscopy (FE-SEM) and non contact atomic force microscopy (NC-AFM) results signify that 3C-SiC film contain well resolved, large number of silicon carbide (SiC) nanocrystallites embedded in the a-Si matrix having rms surface roughness \sim 1.64 nm. Hydrogen content in doped films are found smaller than that of un-doped films. Optical band gap values, E_{Tauc} and E_{O4} decreases with increase in E_{O4} flow rate.

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1. Introduction

Silicon carbide (SiC) is polymorphous with more than 200 different known polytypes. Each SiC polytype exhibits different electrical, optical, and thermal properties due to differences in stacking sequence. Among them nanocrystalline cubic silicon carbide (3C-SiC) possesses unique properties, for instance wide band gap (2.2 eV, at room temperature) [1], high electron drift velocity $(2.0-2.7\times10^7\,\text{cm/s})$ [2], high breakdown field $(2-3\,\text{MV/m})$ [3], high melting point and high thermal conductivity etc. which made it more suitable for many potential applications such as in tandem solar cells, window or buffer layer in amorphous silicon cells [4,5], color sensors [6], thin film light emitting diodes (LEDs) [7], and detecting devices etc. Due to its excellent

chemically stability, it has been used as hard protective coating for harsh environment applications [8]. 3C-SiC films have also been used in fabrication of micro-heaters and resistance thermometer device sensors for micro-electro-mechanical systems (MEMS) [9].

Several techniques are used for the preparation of 3C-SiC films. These include electron cyclotron resonance chemical vapor deposition (ECR-CVD) [10], conventional plasma enhanced chemical vapor deposition (PE-CVD) [11], inductively coupled plasma chemical vapor deposition (ICP-CVD) [12], sputtering [13], and laser ablation [14], photo chemical vapor deposition (Photo-CVD) [15], low pressure chemical vapor deposition (LP-CVD) [9,16] etc. Each deposition method has its own advantages and limitations. The PE-CVD technique has an integration advantage in the device fabrication with the current technologies employed in semiconductor industries but this technique has the problem of ion damage on the growing surface and interfaces because of use of high power density, low deposition rate due to use of high hydrogen dilution and low carbon incorporation efficiency. The ECR-CVD technique

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has the problem of non-uniform deposition over the large area and requires very complicated equipment. Deposition of 3C-SiC layers by sputtering technique requires high substrate temperature (750–800 °C) [17,18]. The LP-CVD technique requires very high substrate temperature of 800–900 °C for the growth of polycrystalline 3C-SiC films. In context of device fabrication, high deposition rate and low substrate temperature are desirable. Thus, search of alternate deposition methods, which allow high deposition rates at low substrate temperature and device quality 3C-SiC films, are enviable.

In recent years, HW-CVD method has emerged as a promising technique to deposit such films at relatively low substrate temperature [19-23]. The two major advantages of employing HW-CVD method for the synthesis of SiC coatings are, first is the absence of the deleterious electrons and ions and surface charges which avoid powder formation and second is high dissociation rate of source gases which leads to higher deposition rate, large area fabrication, deposition rate etc. over other conventional PE-CVD [24]. Furthermore, the microstructure of SiC thin films can easily be tuned by manipulating the deposition parameters. However, capabilities of HW-CVD for obtaining device quality 3C-SiC have not been fully established and few reports on the doped 3C-SiC films exist in the literature. With this motivation we have initiated the study of synthesis of boron doped 3C-SiC by HW-CVD method. In this paper, we present results of investigation of influence of boron doping on electrical, structural, morphological and optical properties of 3C-SiC films deposited by HW-CVD method.

2. Experimental

2.1. Film preparation

Intrinsic and boron doped 3C-SiC films were deposited simultaneously on Corning #7059 glass and c-Si wafers in a locally fabricated HW-CVD system, details of which have been described elsewhere [25]. Films were prepared by using pure SiH₄ as Si source gas, CH₄ as C source gas and B_2H_6 as dopant gas (All, Matheson Semiconductor Grade). The flow rate of SiH₄ and CH₄ are kept constant at 3.5 sccm and 5 sccm, respectively while flow rate of B_2H_6 is varied from 0 sccm to 1.0 sccm. The substrate temperature was held constant during the deposition at the

Table 1Deposition parameters used for the synthesis of boron doped 3C-SiC thin films.

Process parameter	Process value
Filament temperature ($T_{\rm fil}$) Deposition pressure ($P_{\rm dep}$) Substrate temperature ($T_{\rm sub}$) Filament to substrate distance ($d_{\rm s-f}$) Deposition time (t)	1900°C 500 mTorr 350°C 5 cm 25 min

desired value accurately using a thermocouple and temperature controller. Other deposition parameters are listed in Table 1.

The glass substrates were cleaned with double distilled water whereas, the c-Si wafers were etched using solution of HF to remove native oxide layer. The substrates were loaded to the substrate holder and then the deposition chamber was evacuated to the base pressure less than 10^{-6} Torr. Prior to each deposition, the substrate holder and deposition chamber were baked for two hours at $100\,^{\circ}\text{C}$ to remove any water vapor absorbed on the substrates and to reduce the oxygen contamination in the film. After that, the substrate temperature was brought to desired value by appropriately setting the inbuilt thermocouple and temperature controller. The deposition was carried out for desired amount of time and films were allowed to cool to room temperature in vacuum.

2.2. Film characterization

Room temperature dark conductivity (σ_{dark}) was measured by employing a 2400 Keithley source-meter in planar geometry. Temperature dependence conductivity was measured between 210 and 400 K and the activation energy (E_{act}) was calculated from,

$$\sigma = \sigma_0 \exp\left(\frac{E_{\text{act}}}{kT}\right) \tag{1}$$

where k is the Boltzmann constant and T is the absolute temperature. The carrier concentration, charge carrier mobility and hall coefficient were measured using Van der Paw method (Ecopia HMS-3000hall Measurement System). FTIR spectra of the films were recorded by using FTIR spectrophotometer (Shimadzu, Japan). Bonded hydrogen content (C_H) was calculated from

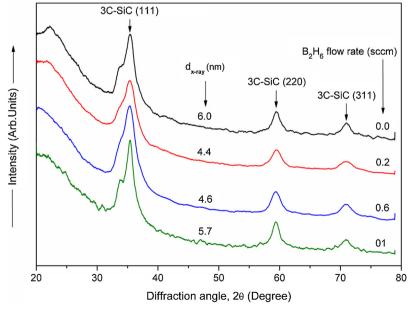


Fig. 1. Low angle XRD pattern of boron doped SiC thin films deposited at different B₂H₆ flow rates.

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