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Amorphous to crystalline phase transition in pulsed laser deposited silicon carbide

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Abstract

SiC thin films were grown on Si (1 0 0) substrates by excimer laser ablation of a SiC target in vacuum. The effect of deposition temperature (up to 950 °C), post-deposition annealing and laser energy on the nanostructure, bonding and crystalline properties of the films was studied, in order to elucidate their transition from an amorphous to a crystalline phase. Infra-red spectroscopy shows that growth at temperatures greater than 600 °C produces layers with increasingly uniform environment of the Si–C bonds, while the appearance of large crystallites is detected, by X-ray diffraction, at 800 °C. Electron paramagnetic resonance confirms the presence of clustered paramagnetic centers within the sp^2 carbon domains. Increasing deposition temperature leads to a decrease of the spin density and to a temperature-dependent component of the EPR linewidth induced by spin hopping. For films grown below 650 °C, post-deposition annealing at 1100 °C reduces the spin density as a result of a more uniform Si–C nanostructure, though large scale crystallization is not observed. For greater deposition temperatures, annealing leads to little changes in the bonding properties, but suppresses the temperature dependent component of the EPR linewidth. These findings are explained by a relaxation of the stress in the layers, through the annealing of the bond angle disorder that inhibits spin hopping processes.

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Keywords: Laser ablation; Silicon carbide; Atomic force microscopy; X-ray diffraction; Infra-red spectroscopy; Electron paramagnetic resonance

1. Introduction

Crystalline silicon carbide (c-SiC) is a wide band gap semiconducting material that has some unique properties making it suitable for the fabrication of devices that can operate under extreme conditions of temperature, frequency, and power, where silicon (Si) based devices would fail. The development of SiC based devices that can sustain harsh environments will impact a multitude of technological fields ranging from the automobile and aerospace industry, to power delivery systems, microwave communications and micro electro mechanical systems (MEMS) [1]. Amorphous silicon carbide (a-SiC) is a form of SiC, in which the long range crystalline order of the material is absent. This material has also found uses in a wide range of applications encompassing microelectronic and optoelectronic devices [2] to protective coatings [3] and membrane material for X-rays lithography [4]. Among the most attractive physical properties of a-SiC are its hardness and Young's modulus, its variable optical gap and its chemical inertness, all of which can be controlled by disorder (either on the atomic or microstructural scale) as well as its hydrogen content and stoichiometry (Si/C ratio) [5]. Several deposition techniques have been used to produce SiC in its crystalline as well as its amorphous forms. Chemical-vapor deposition (CVD) is possibly the most frequently used method for the growth of c-SiC films on Si but it requires high substrate temperatures of about 1200 °C [6] which may degrade interface quality. For the amorphous phase, Plasma-enhanced CVD (PECVD) is predominantly used to grow hydrogenated films (a-SiC:H) [7] while sputtering [3,8] and CVD followed by thermal anneals [2] have been used to obtain unhydrogenated a-SiC. It has been shown recently that such post-deposition anneals, at a temperature of 1000 °C, could significantly reduce the leakage current in the accumulation region of metal–insulator–semiconductor based on magnetron sputtered SiC thin films [9].

Over the last decade, pulsed laser deposition has emerged as a technique that can be utilized to grow epitaxial, polycrystalline

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and hydrogen-free amorphous SiC [10–21]. In most reports, it is found that substrate temperature during film growth is the main parameter that influences the crystallinity and nanostructure of films. Actually, the majority of published work on the PLD of SiC focused on the characterization of crystalline films obtained at temperatures exceeding 800 °C using excimer lasers [12,16,18,19,22] and very recently, using femto-second lasers [23]. There is a general agreement that the polycrystalline cubic phase, 3C–SiC or β-SiC, is obtained at 800 °C and above [11,13,16], though Wang et al. [14] have reported the formation of epitaxially oriented 4H–SiC films on the Si (1 0 0) substrate by PLD followed by annealing at temperatures higher than 1100 °C, while Muto synthesized the α-SiC phase at 1200 °C [24]. Furthermore, El Khakani et al. [20] investigated the growth by PLD of amorphous SiC (a-SiC) films at low temperatures, and reported on the early stages of a densification of the layers at around 650 °C. This was manifested by a transition of the SiC infra-red (IR) absorbance band from a Gaussian to a Lorentzian, and changes in the broadening mechanisms of the electron paramagnetic resonance (EPR) signal that originates from carbon clusters present in the layers [25]. However, the extent of the densification and the transition to fully crystallized layers were not detected because the study was limited to a maximum deposition temperature of 650 °C and therefore, restricted to predominantly amorphous layers. Reitano and Baeri [15] observed a similar transition in the IR spectra of PLD SiC at lower deposition temperature (500 °C) but attributed it to film crystallization, which would be induced at low temperature by the high kinetic energy atoms generated in the laser ablation plume. Moreover, from optical transmission measurements, Rimai et al. [11] reported two distinct deposition regimes: at temperatures above 1000 °C, where the films are highly crystallized with a band gap, E_g, of about 2.25 eV, and below 600 °C for which E_g decreases and the films become amorphous and insulating. From these results, some contradictions appear regarding the temperature at which crystallization of PLD SiC thin films takes place while the mechanisms that govern film densification and crystallization that appear to take place in a deposition temperature range between 500 and 800 °C are still not fully understood.

The goal of this work is to investigate the transition of pulsed laser deposited SiC from an amorphous to a crystallized state, by probing the changes in the nanostructure of the films when deposition temperature, T_d, is varied from 400 to 950 °C and after subjecting the deposited layers to vacuum annealing at a temperature of 1100 °C. The study is performed through the characterization of the deposited layers by grazing incidence X-ray diffraction (GIXRD), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and EPR. Because of the somewhat limited number of studies related to the EPR of a-SiC compared to amorphous carbon materials [26], and since this technique gives information about the IR silent carbon domains, particular emphasis was placed on investigating the behavior of the EPR signal, in terms of spin density, lineshape and temperature dependence, upon the transition of SiC from the amorphous to the crystalline phase and subsequent post-deposition annealing. In addition, the effect of laser intensity on the phase transition was also addressed.

2. Experimental aspects

SiC thin films, with thicknesses ranging from 0.15 to 0.35 μm, were grown by PLD using the SURFACE Laser Workstation based on a KrF excimer laser at a wavelength of 248 nm, a repetition rate of 10 Hz and pulse duration of 20 ns. The laser beam was focused, at an angle of 45°, on a high purity 2 in. polycrystalline SiC ceramic target. In order to guarantee homogeneous target consumption, the target was set to rotate and toggle continuously during the ablation process. Deposition runs were performed at two different laser energies, namely at 200 and 400 mJ with a laser spot on target of 3 mm × 4 mm, leading to laser fluences of 1.6 and 3.2 J/cm^2, respectively. No droplet incorporation in the deposited layers was observed at these fluences.

Single crystal, *n*-doped silicon (1 0 0) wafers (1–10 Ω cm) were used as substrates; these wafers were conventionally cleaned and etched using a 1:1 solution of hydrofluoric acid and deionized water. The substrates were then dried in flowing nitrogen, mounted on a substrate holder, placed parallel to the SiC target at a distance of 5 cm. The chamber was then evacuated to a residual pressure of 10^{-7} mbar using a turbo-molecular pump and the substrate was heated to the desired deposition (T_d) ranging from 400 to 950° C, as measured using a thermocouple embedded in the substrate holder just underneath the substrate. To study the effect of post-deposition annealing on the SiC thin films, square pieces were cut from the samples and were inserted into open quartz tubes of 1 cm in diameter and 10 cm in length. The tubes were then connected to a vacuum system and pumped down to a final pressure of about 10^{-5} mbar, after which the tubes with the samples inside were sealed. Annealing of the samples was achieved by placing these tubes in an oven at a temperature of 1100 °C for 1 h, after which the oven was turned off and allowed to cool with the sample inside.

An automated Discover 8 diffractometer from Bruker AXS systems with an X-ray tube emitting Cu Kα radiation (λ = 1.5418 Å) was used to perform GIXRD measurements on the deposited layers. The incident angle was set at 2° and the detector was scanned from $2\theta = 20°$ to 70°. The data collection and spectral analysis were made using the manufacturer's XRD Commander and EVA software, respectively. The FTIR spectra were acquired using an Avatar 360 spectrometer (Nicolet Instrument Corporation) working in the mid-infrared range from 400 to 4000 cm^{-1}, in the absorption mode with a resolution of 1 cm^{-1} and after baseline correction. The surface morphology of the SiC films was inspected using a MultiMode SPM (NanoScopeIII) from Digital Instruments, in ambient air under contact mode. The EPR measurements were made on a home-assembled spectrometer at X band (9.4 GHz) and Q band (34 GHz) using the Bruker ER041 and ER051 bridges, with a Varian TE_{102} and a Bruker TE_{011} (ER5106 QT) cavities, respectively. The amplitude of the 100 kHz modulating magnetic field was kept below 25% of the signal linewidth (typically 3–8 G for our samples) to avoid over-modulation and broadening of the EPR signal. The incident microwave power was also kept below 1 mW to ensure that the EPR signal is not