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RF plasma reactive pulsed laser deposition of boron nitride thin films

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Abstract

Thin films of boron nitride (BN) have been deposited on Si(1 0 0) substrates by reactive pulsed laser ablation (PLA) of a boron target in the presence of a 13.56 MHz radio frequency (RF) nitrogen plasma. The gaseous species have been deposited at several substrate temperatures, using the on-axis configuration. The film properties have been investigated by Scanning Electron Microscopy, Atomic Force Microscopy, Fourier Transformed Infrared Spectroscopy, and X-ray diffraction characterization techniques, and compared to those resulting from the conventional PLA method. The behavior of hexagonal-BN and cubic-BN phases grown by PLA as function of substrate temperature is also reported.

Keywords: Reactive pulsed laser deposition; RF plasma; Nitrides; Thin films

1. Introduction

Pulsed laser deposition (PLD) technique has proven its ability for obtaining good quality thin films at relatively high growth rate (about 1 nm per pulse), preserving the stoichiometry of the target into the deposit [1,2]. Also, metastable phases can be obtained due to the high energy of species forming the expanding plasma plume. Furthermore, the target ablation in a chemically reactive ambient can lead to the formation of new molecular species which may improve the films features (e.g. crystallinity), even at low substrate temperature. In this paper, in order to enhance the reactivity of the gas phase, a 13.56 MHz radio frequency (RF) generated nitrogen plasma has been used during pulsed laser deposition of BN thin films.

Boron nitride (BN) [3] is one of the most interesting III–V compounds due to its particular properties, such

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as the ability to form strong covalent bonds. This material has a wide range of application in electronics (e.g. gate insulator), nuclear energy and metallurgy as wide gap semiconductor, super-hard coatings (also towards corrosive agents), refractory material, etc. [4–6]. Among the possible crystalline phases, the cubic (c-BN) and the hexagonal (h-BN) ones are the most important. Cubic BN has the second highest room-temperature thermal conductivity and hardness after diamond. Its chemical stability is even better than the one of diamond and it can be used as well to machine ferrous alloys. However, the stable ordered BN phase is the hexagonal sp^2-bonded structure, which has the c-surface with van der Waals' interaction. Therefore, it can be an excellent buffer to promote hetero-epitaxy nanostructure without dangling bonds on the substrate surface material, offering the desired gap at the interface between grown material and the layer having little atomic matching [7].

Several physical and chemical vapor deposition methods have been successfully utilized to prepare BN [6,8,9], and some attempts were made to deposit cubic-BN films by PLD [10–13]. Thick adherent c-BN films are obtained if deposited on top of hexagonal-BN intermediate layer [14].

In this work, we present results regarding the deposition of hexagonal and cubic boron nitride thin films by RF plasma reactive pulsed laser ablation directly from B target in nitrogen atmosphere.

2. Experimental

The experimental set-up has been described in detail elsewhere [15]. The multi-port stainless steel chamber has been pumped down to 10^{-3} Pa, whereas the depositions were performed in static N_2 atmosphere (pressure 10 Pa). A commercial 1 in. diameter boron disk (99.5% purity, Target Materials Inc., Columbus, OH, USA), has been mounted to the rotating holder (2 rpm).

The Quantel Nd:YAG 581 laser ($\lambda = 532$ nm, pulse duration = 7 ns, repetition rate = 10 Hz, fluence = 8 J/cm^2) was impinging on the target at 45° with respect to the normal. The gaseous species were collected on heated Si(1 0 0) substrates (temperature in the range 300–1000 K) positioned 3 cm far away from the target in the on-axis configuration. The PLD set up has been improved by employing a RF generator (13.56 MHz ENI Model OEM-6A, maximum power output 650 W). The RF plasma was placed just above the substrate holder, which was electrically connected to the ground. The substrate holder is surrounded by an isolated stainless steel ring concentric to the substrate holder and connected to the RF generator through a customized matching unit. A diagram of the set-up is reported elsewhere [16].

The samples characterization was accomplished by using different diagnostic techniques. A Leica Cambridge Stereoscan 440 Scanning Electron Microscope (SEM) was utilized to investigate the surface morphology of the deposited thin films, while the topography was investigated by an Atomic Force Microscope Quesant instrument, model Nomad, working in air, in contact mode. X-ray spectra were detected by a Rigaku Miniflex diffractometer using as X-ray source the CuK_α line ($\lambda = 0.154056$ nm). The Fourier Transform Infrared Spectroscopy spectra (FTIR) have been obtained by means of a Nicolet Impact 400 Spectrometer working in transmittance mode and 4 cm^{-1} spectral resolution.

3. Results and discussion

3.1. Surface characteristics

Scanning Electron Microscopy and Atomic Force Microscopy have been employed to study the thin films surface morphology. The improvement of the surface quality even for low substrate temperature by assisting the PLD deposition with the RF plasma has been previously shown [17]. A micrograph of a RF plasma-aided boron nitride sample, deposited on Si(1 0 0) at 800 K substrate temperature is presented in Fig. 1. It can be seen that by employing higher deposition temperatures, the film surface becomes smoother, even though it is still covered by droplets of different dimensions. In order to obtain in deep information regarding the surface characteristics, the AFM scan performed over an area of 5 μm × 5 μm is reported in Fig. 2. The average height of the investigated area is around 100 nm, while the rough mean square deviation is 26.3 nm. The distribution of the particulates with diameters in the range 200–500 nm present on the surface of BN film deposited at