Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 514 (2006) 138 – 144
www.elsevier.com/locate/tsf

On the nucleation of the cubic phase in boron nitride films

Jian Ye, Hans Oechsner *

Department of Physics and Institute for Surface and Thin Film Analysis, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

Received 9 June 2005; received in revised form 27 February 2006; accepted 28 February 2006
Available online 4 May 2006

Abstract

Boron nitride films were produced on silicon substrates by r.f. magnetron sputtering with pure argon as working gas. The cubic BN (*c*-BN) phase was achieved through an r.f. substrate bias which set up a controlled ion bombardment on the growing surface. The dependence of film structure on the deposition time was studied at fixed growth parameters by means of Fourier transform infrared spectroscopy, Auger electron spectroscopy, low energy electron loss spectroscopy, atomic force microscopy, and ellipsometry. The results show for the first time that the nucleation into *c*-BN takes place through a phase transformation process of the upper part of an *h*-BN base layer formed in the initial growth stage. Special features correlating with this transformation are presented, particularly a shrinking of the film's volume and a transient extraordinarily high roughness of the growing surface. The results indicate that *c*-BN nucleation is not directly governed by the instantaneous ion bombardment of the growing film.

PACS: 52.77.Dq; 81.15.Cd; 68.55.Nq
Keywords: Boron nitride films; Nucleation and film growth; Electron spectroscopy; Ion assisted deposition

1. Introduction

Novel and qualified materials for hard and superhard protective coatings are constantly required for numerous industrial applications. Such demands have stimulated much interest in the deposition of cubic boron nitride (*c*-BN) films through PVD and CVD techniques due to the outstanding properties of this material [1–8].

In spite of successful implementation of various deposition methods (for a recent review cf. to Ref. [9]) the understanding of the growth mechanism of the *c*-BN-phase is still not satisfactory. Several models have been developed in the past which are primarily based on the research on tetrahedrally configurated carbon films [10,11] and which necessitate a moderate ion bombardment of the growing film. Representative model considerations include selective sputtering of the hexagonal phase [12], densification of growing film by subplantation processes [13], and stress-induced formation of the tetrahedral or cubic phase [14,15]. For ion assisted deposition of pure BN- films one of the most attractive features concerns the initial structural evolution [16–19] which was first illustrated by Kester et al. [16] and more recently also in our own studies [20] through high-resolution TEM images. It starts off with an amorphous BN layer next to the substrate which then transfers to a layer of highly oriented hexagonal BN (*h*-BN) with the c-axis parallel, i.e. the (0002) plane normal to the film plane[1], and ends up with *c*-BN. The evolution of such structures takes place amazingly under constant ion bombardment during the deposition, which may indicate an influence of the existing actual film structure on the formation of the next phase. In this regard a few disparate suggestions have been proposed which refer, for instance, to a possible lattice matching between *c*-BN and the host matrix on the growing surface [5,21,22], or to the high compressive stress in the near-surface region of the textured *h*-BN which within the frame of McKenzie's model [14] could result in the formation of the cubic BN-phase.

Hence, for further clarification experimental studies on the nucleation process of *c*-BN appear necessary. The present paper reports on detailed observations of corresponding phenomena during the initial stage of the deposition of BN-films by r.f. magnetron sputtering with a controlled substrate bias.

---

* Corresponding author. Tel.: +49 631 205 4029; fax: +49 631 205 4301.
E-mail address: hoe@rhrk.uni-kl.de (H. Oechsner).

[1] *h*-BN with such a texture is sometimes assigned as turbostratic BN (*t*-BN).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.02.097

2. Experimental details

The deposition of boron nitride films was carried out in a home-made r.f. (27.12 MHz) magnetron sputtering system, using (100)-oriented silicon substrates and an *h*-BN target. Argon was employed as the working gas. The substrate electrode was independently connected to a second r.f. generator (also operated at 27.12 MHz) to establish a negative dc self-bias voltage at the substrate with the growing film. The ion energy at the substrate was measured by a retarding field analyzer which separates the ion component from the superimposed flux of plasma electrons. The base pressure was in the low 10^{-6} mbar-regime. For more details of the experimental setup see Ref. [7].

The r.f. power at the *h*-BN sputter target (60 mm in diameter, 1 mm thick) was fixed at 400 W, the substrate temperature, the self-bias voltage at the substrate and the working pressure (Ar) were always 600 °C, 200 V and 3×10^{-3} mbar, respectively. The ion current density at the substrate was around 1 mA/cm^2. These growth parameters were found to promote the synthesis of *c*-BN films for the present deposition system, leading to volume fractions of the cubic phase of more than 85% as derived from the infrared (IR) spectra probing the entire films with a thickness of or below 200 nm. (Fig. 1).

In order to study the evolution of the individual BN-phases mentioned in the introduction, a large number of films have been deposited for increasing and precisely controlled growth times. The thickness of each individual film was determined by spectroscopic ellipsometry. Atomic force microscopy (AFM) has been used to investigate the surface morphology. The average ratio between the hexagonal and the cubic phase in the films was evaluated through Fourier Transform Infrared Spectroscopy FTIR in the transmission mode by the absorption intensities of the *h*-BN in-plane stretching mode at 1390 cm^{-1} and the *c*-BN transverse optical (TO) mode near 1100 cm^{-1}, respectively (cf. Fig. 1). Surface sensitive techniques as Auger electron spectroscopy (AES) and low energy electron loss spectroscopy (LEELS) [23] were adopted to provide supplementary information on the phase evolution in the near-surface region. The structure identification by AES was based on a satellite peak of the B (KLL) transition at 182 eV that is indicative of *h*-BN [23,24]. In LEELS, *h*-BN and *c*-BN were distinguished from their characteristic plasmon losses and the specific energy loss due to the $\pi \rightarrow \pi^*$ electron excitation in *h*-BN. These characterization methods enabled a reliable discrimination between *h*-BN and *c*-BN in the deposited films with carbon and oxygen contents well below 3 at.% (Fig. 2).

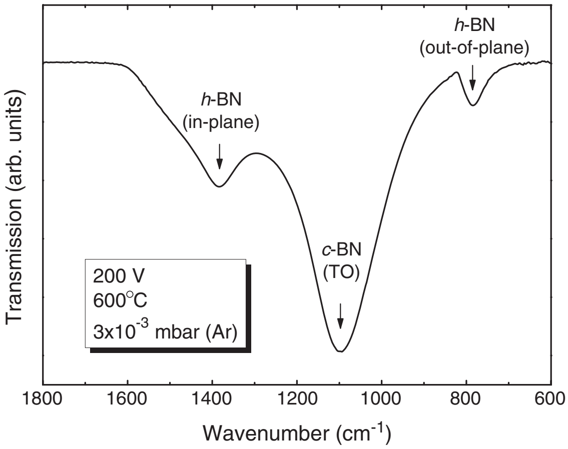

Fig. 1. Infrared spectrum of a 200 nm *c*-BN film deposited at 3×10^{-3} mbar Ar, 200 V substrate bias, and 600 °C substrate temperature. The cubic phase fraction is about 85% as estimated from the absorption intensities of *c*-BN TO-mode near 1100 cm^{-1} and *h*-BN in-plane stretching mode at 1390 cm^{-1}.

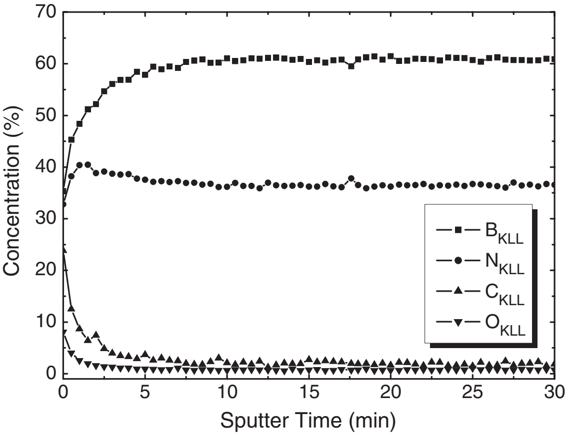

Fig. 2. Auger sputter depth profile (1 keV Ar$^+$, 10 μA/cm^2) of a BN film.

3. Experimental results[2] and discussion

3.1. Structural evolution

Fig. 3(a) displays the differentiated electron spectra of the B (KLL) Auger transition for the BN-films produced with different deposition times. The surface sensitive Auger spectra were intentionally taken without sputter cleaning of the films' surfaces. For the samples with short deposition times up to 5 min, the *h*-BN-specific peak at 182 eV is clearly observed. This characteristic detail of the peak structure disappears almost completely for deposition times above 6 min. Such a shape variation of the Auger peak can be clearly attributed to the transition from initial *h*-BN growth to the formation of almost pure *c*-BN. Additional evidence is given in Fig. 3(b) through the electron energy loss spectra associated with the ionization of the boron K-shell under irradiation with 800 eV-electrons, probing again the near surface region. The π^*-feature at 193 eV, which disappears also at deposition times above 6 min, results from the existence of π-electrons and is, therefore, pertinent to the sp^2-hybridization in *h*-BN crystallites. Since for any longer growth time this feature cannot be detected at all, a *c*-BN surface layer with a thickness of at least the penetration range of the exciting electrons with a mean inelastic free path length of about 3 nm must have been established on top of the previously formed *h*-BN base layer. According to the deposition times given in the figures, the transition to *c*-BN-growth occurs in a time interval around 5 min for the experimental parameters employed in the present study.

---

[2] First presented at the Internat. Conf. on Metallurg. Coatings and Thin Films ICMCTF 2001, San Diego (USA).