Available online at www.sciencedirect.com

Applied Surface Science 247 (2005) 45–50

applied surface science

www.elsevier.com/locate/apsusc

Number density and size distribution of droplets in KrF excimer laser deposited boron carbide films

T. Szörényi [a,b,*], R. Stuck [a], F. Antoni [a], E. Fogarassy [a]

[a] CNRS-PHASE, BP 20, 67037 Strasbourg Cedex 2, France
[b] Research Group on Laser Physics of the Hungarian Academy of Sciences,
University of Szeged, PO Box 406, H-6701 Szeged, Hungary

Abstract

This paper contributes to the old problem of droplet formation by providing detailed quantitative data on the population statistics of particulates deteriorating the surface of boron carbide films produced by PLD. Films of 180 ± 30 nm thicknesses have been fabricated by KrF excimer laser ablation of a sintered B_4C target in high vacuum. Number densities and size distributions of the particulates are given for 14 films, deposited at laser fluences tuned between 2 and 14 J cm^{-2}, as a result of evaluating SEM images of the same magnification taken from minimum five different areas (altogether $(2–4) \times 10^{-2}$ mm^2) of each film. The overwhelming majority of the droplets is small with diameters, $d \leq 1$ μm. The number density of those with $d \leq 0.5$ μm ranges from (1 to 7) × 10^4 mm^{-2}. The effect of gradual deterioration of the target surface as a result of prolonged irradiation screens practically totally the effect of changing fluence. The number of droplets of diameters in excess of 1 μm increases linearly with increasing number of shots/site resulting in maximum surface coverage values as high as 36%.

Keywords: PLD; Thin films; Boron carbide; B_4C; Particulates; Droplets; Size distribution; Histograms

1. Introduction

The binary and ternary compounds of the boron–carbon–nitrogen (BCN) triangle possess unique combinations of extreme properties. Boron carbide, B_4C is one of the hardest materials known. It is semiconducting with high melting point and high resistance to wear and chemicals. While being a prerequisite of many practical applications, fabrication of boron carbide in thin film form remained a challenge. During recent years pulsed laser deposition, PLD matured to a well established laboratory technique for pilot production of thin films of materials hard to handle with more conventional approaches [1]. However, critical analysis of the results reported up to now on the fabrication of boron carbide films by PLD are inadequate and, in some ways, inconsistent [2–7]. The two critical issues are stoichiometry and droplets. In this paper we focus on the problem of droplets.

Kokai et al. [2,3] ablated a sintered B_4C target with a YAG laser (fourth harmonic: $\lambda = 266$ nm, $\tau = 4–$

---

* Corresponding author. Tel.: +36 62 544274; fax: +36 62 544658.
E-mail address: t.szorenyi@physx.u-szeged.hu (T. Szörényi).

0169-4332/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2005.01.092

5 ns, 10 Hz) at a pressure of $<1.3 \times 10^{-4}$ Pa. The target-to-substrate distance was 30–50 mm. Scanning electron microscopy revealed the presence of particulates of sizes ranging from 0.5 to 5 μm embedded in the films. Both the shape and density of these depended on the fluence. A thorough analysis of the SEM micrograph presented in Fig. 1a of Ref. [2] suggests that the analysis of the low fluence case (1.1 J cm^{-2}) put forward by the authors remained incomplete. The particulate number density figure given for the irregularly shaped particulates ($\sim 4 \times 10^3$ mm^{-2}) seems to be realistic. This estimation is further supported by the histogram referring to the 1.1 J cm^{-2} case reported by the same authors in another paper (Fig. 2a in Ref. [3]). However, the authors failed to mention the appearance of droplets, exceeding in number the particulates. The much lower figure reported for 3.0 J cm^{-2} ($(1\text{–}5) \times 10^2$ mm^{-2}) is well supported by Fig. 1b of Ref. [2].

Shin-ichi Aoqui et al. ablated a similar target with 2 and 5 J cm^{-2} pulses of a KrF excimer laser [4]. Their observation that for target-to-substrate distances higher than 40 mm no real films, only particles adhering onto the substrate could be deposited, underlines the role of the particulates in controlling film growth in this case. The surface roughness analyzer images (Figs. 3 and 4 in Ref. [4]) clearly show that ablation of the sintered B_4C target has actually resulted in films with unusually rough surface due to high density of droplets of diameters within the 0.5–5 μm range. One must not be misled by the 0.19 nm roughness value reported [4]. This unrealistically low figure exemplifies that without definition, details of the measurement procedure and, most importantly, the dimensions of the measured area average roughness values have no real meaning.

AFM scans over 5 μm × 5 μm areas exemplify that ~40 nm thick boron carbide films grown by ablating a sintered B_4C target in 2×10^{-4} Pa with 5 J cm^{-2} pulses of a Nd:YAG laser (second harmonic, 5 ns, 10 Hz) possess a smooth continuous surface with relatively high number density ($>10^6$ mm^{-2}) of submicrometer particulates [6].

Dietsch and coworkers also report on successful deposition of good quality ultra-thin films of boron carbide as components of Ni/B_4C and Mo/B_4C multilayer stacks of 3.74 and 3.50 nm periods, respectively, by optimizing their YAG-based ($\lambda = 1064$ nm) PLD technology [7]. The message of this paper is that PLD can be scaled up to cover substrates up to 6 inches in diameter meeting the extremely stringent requirements of X-ray optics fabrication. Material issues are not detailed.

Our paper contributes to the old problem of droplet formation by providing detailed quantitative data on both number density and size distribution of particulates deteriorating the surface of boron carbide films produced by PLD. The results reported confirm that droplet formation may cause serious problems when ablating a sintered B_4C target, indeed.

2. Experimental details

Films of 180 ± 30 nm thicknesses were deposited onto Si(1 0 0) wafers by ablating a hot pressed B_4C target (CERAC), rotating at ≈1 rpm, with a KrF excimer laser (248 nm, 10 Hz, maximum 320 mJ/pulse) at a pressure of $(1\text{–}2) \times 10^{-5}$ Pa, at room temperature, by keeping the deposition time × laser fluence product constant. The target-to-substrate distance was set to 48 mm and the energy density on the target surface was varied between 2 and 14.3 J cm^{-2}.

Changes in the lateral dimensions and the number of particulates on the surface of the films were followed by a JEOL JSM-35CF scanning electron microscope. Minimum five pictures, one in the middle of the sample and four others approx. halfway between the centre and the edges were taken on all samples. In order to ensure comparability, the same magnification (1000×) was used throughout the whole measurement series, keeping all other parameters fixed. Since due to multiple overlaps and differences in the appearance of the droplets (cf. Fig. 1) all standard computer codes examined failed, all SEM micrographs were evaluated manually. 100 μm × 100 μm and 20 μm × 20 μm surface areas were scanned by a TopoMetrix 2000 atomic force microscope in contact mode, keeping the force applied by the stylus to the sample constant.

3. Results and discussion

Two series of films have been deposited. Within each one the position of the laser beam remained fixed