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Influence of deposition temperature on the structural and morphological properties of Be_3N_2 thin films grown by reactive laser ablation

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ABSTRACT

Be_3N_2 thin films have been grown on Si(1 1 1) substrates using the pulsed laser deposition method at different substrate temperatures: room temperature (RT), 200 °C, 400 °C, 600 °C and 700 °C. Additionally, two samples were deposited at RT and were annealed after deposition *in situ* at 600 °C and 700 °C. In order to obtain the stoichiometry of the samples, they have been characterized *in situ* by X-ray photoelectron (XPS) and reflection electron energy loss spectroscopy (REELS). The influence of the substrate temperature on the morphological and structural properties of the films was investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). The results show that all prepared films presented the Be_3N_2 stoichiometry. Formation of whiskers with diameters of 100–200 nm appears at the surface of the films prepared with a substrate temperature of 600 °C or 700 °C. However, the samples grown at RT and annealed at 600 °C or 700 °C do not show whiskers on the surface. The average root mean square (RMS) roughness and the average grain size of the samples grown with respect the substrate temperature is presented. The films grown with a substrate temperature between the room temperature to 400 °C, and the sample annealed *in situ* at 600 °C were amorphous; while the αBe_3N_2 phase was presented on the samples with a substrate temperature of 600 °C, 700 °C and that deposited with the substrate at RT and annealed *in situ* at 700 °C.

1. Introduction

The study and production of semiconductor materials with wide-band gap in the ultraviolet region have received notorious attention, due to their potential for the development of applications in devices of illumination and communication. In the last few years, semiconductor materials with nanostructure as nanowires and nanowhiskers have received much interest by their possible applications in optoelectronic nanometric scale devices [1]. It has been reported that beryllium nitride Be_3N_2 presents optical properties that makes it a candidate for applications in the extreme UV and soft X-rays [2]. The Be_3N_2 has two crystallographic structures, cubic αBe_3N_2 and hexagonal βBe_3N_2 [3–5]. The cubic structure is stable between 20 °C and 1200 °C and for temperatures over 1400 °C the hexagonal phase appears. Beryllium nitride has been deposited by different techniques including sputtering [6,7] and laser ablation [8]. In the literature, the properties of B_3N_2 thin films at room temperature [6,7] and 750 °C [8,9] has being reported. However, to our best knowledge, there are no reports of the variations of the structural and morphological properties as a function of the substrate temperature. In this work, we present the results of the structural and morphological properties of Be_3N_2 thin films obtained by pulsed laser deposition technique at different substrate and annealing temperatures.

2. Experimental details

Be_3N_2 thin films were grown on Si(1 1 1) substrates using the pulsed laser deposition in a RIBER LDM-32 system equipped, with *in situ* X-ray photoelectron spectroscopy (XPS). The laser utilized for the deposits is a KrF excimer (λ = 248 nm). Laser energy, number pulses and pulse repetition rate were fixed at 200 mJ, 27,000 pulses and 5 Hz, respectively. We used a target of beryllium foil (99.9%) obtained from Alfa Aesar. Ablated material was collected on a series of Si(1 1 1) substrates maintained at room temperature (RT), 200 °C, 400 °C, 600 °C and 700 °C during deposition these samples the N_2 pressure was 25 mTorr. Additionally two samples were deposited at room temperature with the same pressure of

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nitrogen and were annealed *in situ* after deposition at 600 °C and 700 °C for 2 h in a nitrogen pressure of 5 mTorr. Reflection electron energy loss spectroscopy (REELS) spectra were collected using an electron beam with incident energy of 2 and 1 keV, respectively. XPS measurements were obtained using the Al Kα line of an X-ray source with energy of 1456.6 eV. The thin films thickness was measured using a perfilometer model DekTak. The surface morphology of the Be_3N_2 thin films was characterized using scanning electron microscopy (SEM) model Jeol-5300 and atomic force microscopy model nanoscope III, in contact mode. The X-ray diffraction was performed in a Philips X'pert MPD system using Cu Kα X-ray radiation source (λ = 1.5405 nm). Diffractograms were recorded from 20° to 80° with a step of 0.01°.

3. Results and discussion

All samples were uniform, without holes and firmly adhered to the substrate. The thin film thickness obtained was of 150 ± 10 nm, for all growing conditions. The Be_3N_2 thin films were characterized *in situ* by XPS and all films showed signals corresponding to beryllium, nitrogen and oxygen. Fig. 1 shows a typical XPS spectrum of Be_3N_2 thin films deposited in this work and the concentration of oxygen in the samples were lower than 10 at.%. The presence of a small amount of oxygen probably can be attributed to a spurious source during the growth process like residual water in the nitrogen introduction tubing lines. The intensity of the oxygen peak was about similar in all films. Soto et al. [8], using also the pulsed laser deposition technique in an experimental setup similar to our work, show the beryllium-nitrogen reaction to be completed when the beryllium nitride is deposited at 25 mTorr of nitrogen pressure and they obtain the stoichiometry of Be_3N_2. In this work, using the same procedure for calculating the stoichiometry as Soto et al., all our thin films present the same Be_3N_2 stoichiometry.

No appreciable changes in the bulk plasmon position can be distinguished as a function of temperature for the REELS spectra shown in Fig. 2 for films deposited at RT, 400 °C, 600 °C and 700 °C. The maximum at 22.9 eV is similar to the reported value in a previous letter [10]. Also, we can observe a shoulder at 9.6 eV that corresponds to a surface plasmon of a dielectric film [10]. Considering the bulk plasmon energy we calculated the electronic and mass densities, ρ_e and ρ_m, using the method described by Soto et al. [11]. Since the plasmon energy is about the same for all samples, we obtain corresponding values of $\rho_e = 3.9 \times 10^{23}\,cm^{-3}$ and $\rho_m = 2.9\,g\,cm^{-3}$. It is notorious the fact that beryllium nitride samples prepared at different temperatures present about the same electronic and mass densities, particularly since they present

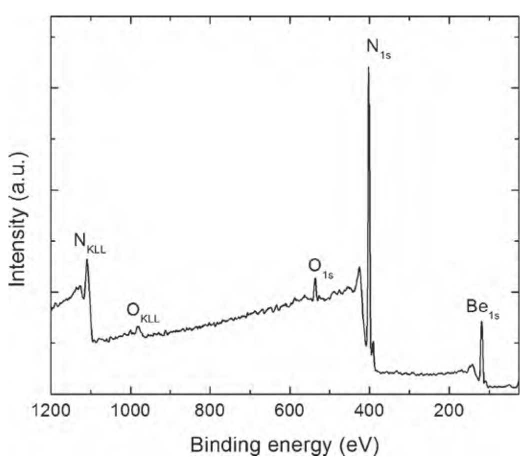

Fig. 1. XPS spectrum of the film grown at a nitrogen pressure of 25 mTorr and substrate temperature of 700 °C.

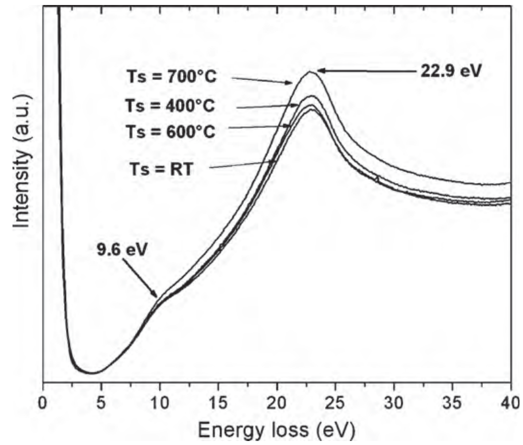

Fig. 2. REELS spectra of Be_3N_2 thin films, deposited at substrate temperature of: RT, 400 °C, 600 °C and 700 °C.

diverse degrees of crystallinity. On the other hand, the mass density for stoichiometric Be_3N_2 calculated considering the atomic weights and unit cell is $2.71\,g\,cm^{-3}$, in good agreement with our results.

Fig. 3, left side, presents SEM images of the observed morphologies for Be_3N_2 samples deposited at substrate temperatures of (a) RT, (b) 400 °C, (c) 600 °C and (d) 700 °C. The film deposited at room temperature shows a smooth surface. The surface of the film grown at a substrate temperature of 600 °C presents formation of whiskers and for the corresponding one at 700 °C, the whiskers have lengths of 1–2 μm and diameters of 100–200 nm. The right side of Fig. 3 shows an AFM sequence of images of thin films grown at different substrate temperature. The film grown with a substrate temperature of 700 °C presents formation of abundant whiskers on the surface with length between 1 and 2 μm. In the AFM image is possible to appreciate that whiskers can grow with a tendency to certain orientations, although not very well defined. Although the mechanism of formation of Be_2N_3 whisker is currently unknown, it is evident the influence of the substrate temperature. One possibility is the formation of nodular particles which promote the whisker formation [12], this phenomena could be enhanced with increasing the substrate temperature.

The average grain size and average RMS roughness value for the deposited Be_3N_2 films increases with substrate temperature, as shown in Table 1. The data was gathered using the contact mode of the AFM system. A substantial change in the value of roughness when the substrate temperature changes from 400 °C to 600 °C is observed, increasing from about 1 nm for temperatures of 400 °C to about 28 nm for 600 °C. The grain size of the Be_3N_2 thin films is small when the substrate temperature is below 600 °C, and about 3 and 9 nm for samples deposited at RT and 400 °C, respectively. However, when the substrate temperature reached 600 °C, the average grain size increased sharply and, at a substrate temperature of 700 °C, the average grain size reaches 49 nm. It is worth to notice the fact that the RMS roughness of the Be_3N_2 thin films deposited with

Table 1
Average grain size and average RMS roughness value for the deposited Be_3N_2 thin films.

Substrate temperature	Average grain size (nm)	RMS roughness (nm)
RT	3.81 ± 0.64	1.31 ± 0.45
400	9.10 ± 0.97	2.67 ± 0.77
600	32.15 ± 1.34	28.73 ± 3.44
700	49.45 ± 5.94	45.09 ± 8.52
RT with annealing of 600 °C	20.22 ± 2.86	2.40 ± 0.18
RT with annealing of 700 °C	33.30 ± 3.53	4.28 ± 0.80

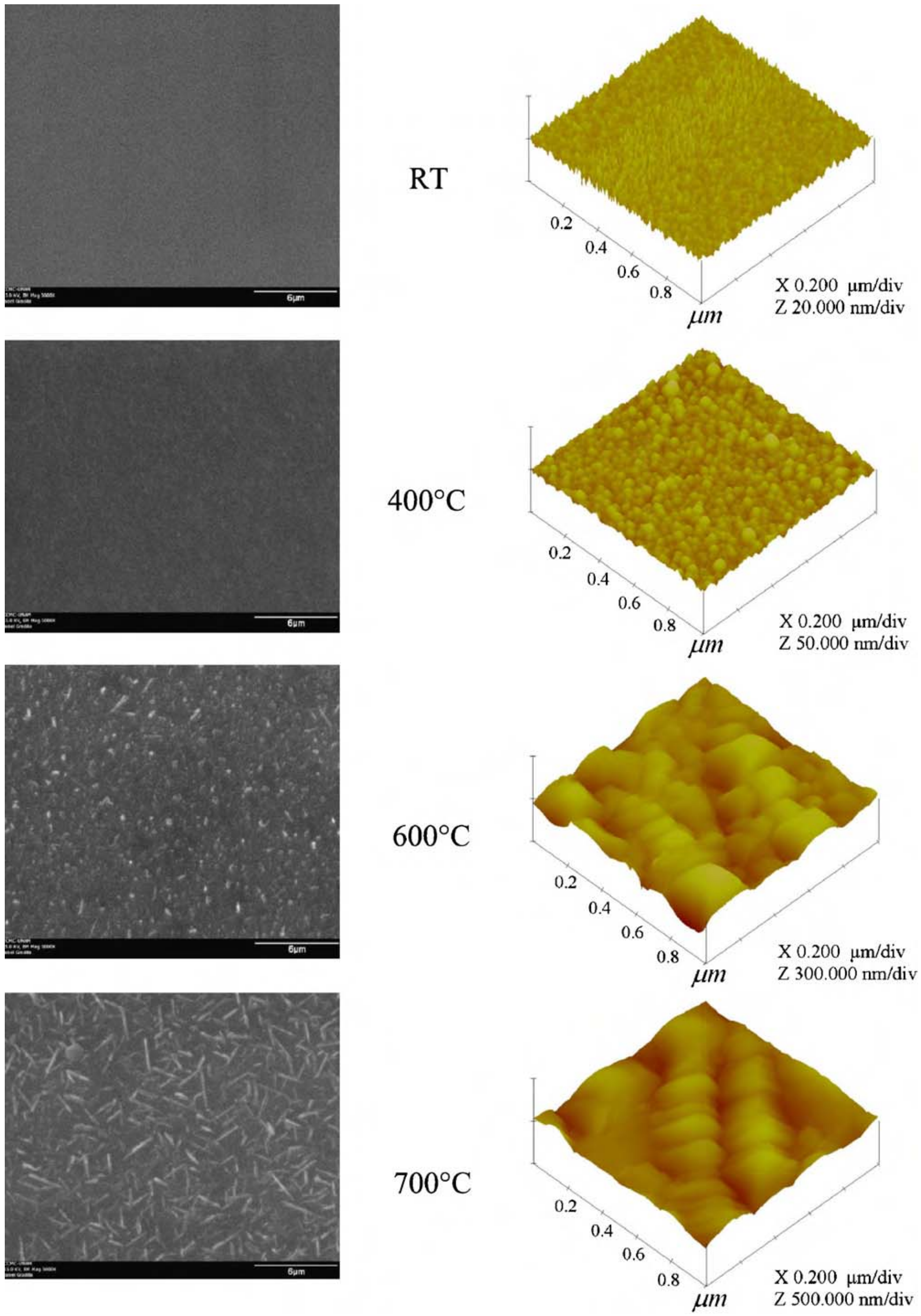

Fig. 3. Sequence of SEM images (left side) and AFM images (right side) of samples deposited at a substrate temperature of: RT, 400 °C, 600 °C and 700 °C.

annealing *in situ* remains with a low value, in spite of the high temperature treatment, while the presented grain size of these samples is relatively high. A similar behavior for the average grain size and surface roughness, with respect the substrate temperature and vacuum annealing has been reported [13,14] for thin films prepared by PLD technique. Also, it can be noticed that, differently from those samples grown at high temperature, the AFM images for Be_3N_2 thin films with *in situ* annealing, presented in Fig. 4, do not show whiskers on the surface.

XRD patterns for the beryllium nitride thin films deposited at RT, 400 °C, 600 °C, and 700 °C and simulated pattern of αBe_3N_2 are presented in Fig. 5. The patterns were indexed using the powder diffraction database files [15]. The samples at 600 °C and 700 °C show diffraction peaks at 38.01° and 50.99°, corresponding to (2 2 2) and (4 2 0) respective planes, characteristic of the αBe_3N_2 phase. The beryllium nitride films grown at RT and 400 °C were amorphous and the corresponding XRD patterns present only the silicon substrate peaks.

Fig. 6 presents XRD patterns of the αBe_3N_2 phase thin films which were grown at room temperature and afterwards were annealed *in situ* during 2 h in nitrogen atmosphere at (a) 600 °C and (b) 700 °C. We observe diffraction peaks at 38.02° and 52.78° corresponding to (2 2 2) and (3 3 2) planes of Be_3N_2 [15], respectively. The XRD pattern of the thin film with annealing at 600 °C do not present any peak corresponding to αBe_3N_2 and only shows peaks associated to the silicon substrate.

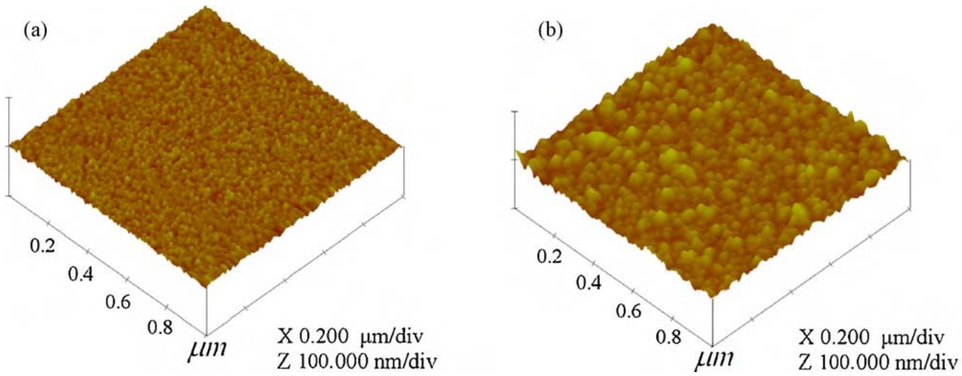

Fig. 4. AFM images of Be_3N_2 thin film with annealing *in situ* at (a) 600 °C and (b) 700 °C.

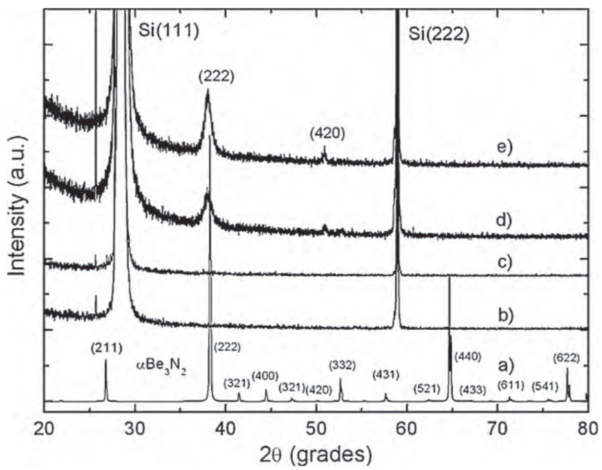

Fig. 5. XRD patterns of Be_3N_2: (a) simulated and deposited at (b) RT, (c) 400 °C, (d) 600 °C and (e) 700 °C.

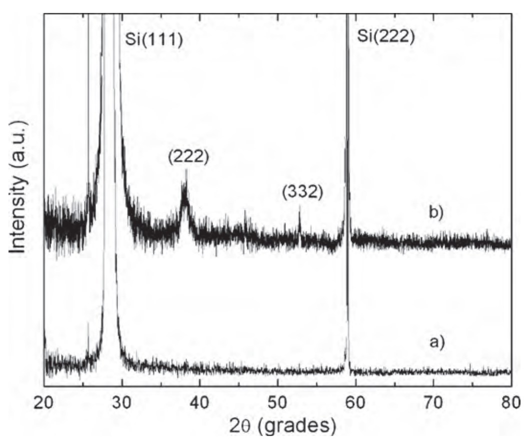

Fig. 6. XRD pattern of αBe_3N_2 thin film deposited at RT and posterior *in situ* annealing during 2 h at (a) 600 °C and (b) 700 °C.

4. Conclusions

The substrate temperature, as well as a subsequent annealing temperature, during processing of Be_3N_2 thin films is very important for determining their structural and morphological properties. The thin films grown at RT and 400 °C are amorphous, and those grown at 600 °C and 700 °C present the αBe_3N_2 phase. There is formation of whiskers on the surface of Be_3N_2 thin films when the substrate temperature is raised to 600 °C or 700 °C. The roughness value changes from about 1 nm, for the sample grown at RT, to about 45 nm, for the sample grown at 700 °C. The thin film deposited at RT with *in situ* subsequent annealing at 700 °C allows obtaining the αBe_3N_2 phase and do not show formation of whiskers, the grain size was relatively high, about 33 nm, and presents a relatively low roughness, of about 4 nm. The Be_3N_2 thin films that presented certain crystallinity, also presented a relatively high grain size, over 30 nm. Substrate temperature does not modify appreciably the electronic or mass densities of the beryllium nitride thin films.

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