Epitaxial α-Be$_3$N$_2$ thin films grown on Si substrates by reactive laser ablation

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Abstract

Beryllium nitride thin films were grown on (111) and (100) silicon substrates by laser ablating a beryllium foil in molecular nitrogen ambient from room temperature up to 900°C. Scanning (SEM) and transmission electron (TEM) microscopies, x-ray diffraction (XRD), auger (AES) and x-ray photoelectron (XPS) spectroscopies characterized the films. The epitaxy of the films was achieved at substrate temperatures of 750°C on (111)-Si. The diffraction measurements are in agreement with the α-Be$_3$N$_2$ phase. The orientation relationship between film-substrate correspond to $[110]//[2\bar{1}0]$ and $(1\bar{1}1)//(\bar{1}2\bar{3})$.

1. Introduction

There is a great interest to develop new semiconductor materials to use them in optoelectronics devices in the blue/ultraviolet spectral region. The extent of the gap and whether it is direct are the most important figures of merit for that application. Unluckily, most of the wide-band-gap semiconductors have indirect band gaps. The only viable semiconductors that fulfill those two requirements appear to be wurtzite *AlN* (6.2 eV) and the related *Ga$_x$Al$_y$N* alloys. Then, a semiconductor with a direct band-gap well into the UV range would clearly be of immense importance to use it alternatively to aluminum and aluminum-gallium nitrides.

Recently our group has put attention on beryllium nitride. There are two recognized crystallographic structures of it: the cubic *α-Be$_3$N$_2$*, with 40 atoms per primitive cell and the hexagonal *β-Be$_3$N$_2$*, with 10 atoms per cell. The latter can be obtained by heating up the cubic phase at *1400°C*. We found, by ab-inito Hartree-Fock self-consistency calculations that both phases have a wide-band-gaps amongst 4 to 5 eV [1,2]. In addition, the gap of the *α-Be$_3$N$_2$* phase is direct, making it an attractive material to develop high-power light emitting devices [3]. However, to arrive at that stage is necessary to do some fundamental research to reveal the practicability of synthesis for a realistic use.

In a past letter we showed that the beryllium-nitrogen reaction is total by ablating a beryllium foil in molecular nitrogen ambient at room temperature, producing a high quality, stoichiometrical accurate amorphous beryllium nitride film [4]. In this occasion, we are interested in showing that the crystallinity of the films can be attained by high temperature treatment during the growth process. With this aim we made an experimental series where the deposition temperature was the strategic test-parameter.

2. Experimental

The films processing were handled in a modified laser ablation system, Riber LDM-32, with *in-situ* AES and XPS facilities. The deposition was accomplished by ablating a 99.9% beryllium foil in the background of high-purity molecular nitrogen. Nitrogen pressures, P_N, where in the $1 \leq P_N \leq 100$ mTorr limits. The substrate temperature, T_S, was fixed for the period of deposition in the room temperature (RT) to *900°C* range, following by a slow cool-down. We made use of as-provided (111) and (100) *n*-doped silicon wafers as substrates, i.e., without any cleaning process. To avoid the incorporation of oxygen the base pressures was keep in *10^{-10} torr* range. Ablation was accomplished by means of a *KrF* excimer laser ($\lambda = 248$ nm) focused on the target at *50°* off the surface normal. Laser energy, number of pulses and pulse repetition rate were fixed

at *400 mJ*, *3800* pulses and *2 Hz*, respectively, for a laser energy density at target surface of *5 J-cm^{-2}*.

Samples were prepared for transmissions electron microscopy by mechanical thinning followed by Ar^{+} ion milling. The specimens were examined in a JEOL 4000EX TEM operating at *400kV*. The XRD was performed in a Philip's X'pert –MPD system using Cu K$_\alpha$ x-ray radiation source (*λ=0.15405 nm*).

3. Results and discussion

In a precedent letter we showed that the critical pressure to accomplish a stoichiometrical correct film at T_S = RT in our experimental system is P_N = *25 mTorr* [4]. Figure 1 shows the *in-situ* auger spectrum of the film deposited at this particular P_N, although now at T_S = *750°C*. As it can be noticed, the films are composed of *Be* and *N*, whereas *O* was observed as a minor impurity element, ~ *2 at %*. A quantitative XPS analysis confirmed that the stoichiometric relation, *N/ Be*, is in agreement with our earlier results, giving the theoretical value of *2/3*.
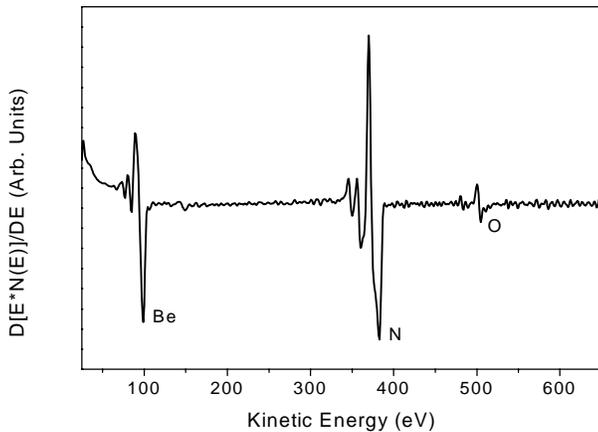
Fig 1.- AES spectrum for the film grown at P_N = 25 mTorr and T_S = 750°C

Subsequently, the substrate temperature does not disturb the stoichiometry of the film significantly. The Be_{KVV} transition is comparable to those that have been previously reported for *Be$_3$N$_2$* [5]. The scanning electron micrographs of the same sample, figure 2, revealed the existence of an uninterrupted homogeneous film, in addition to large rod-shaped islands and the splashing typically found in films processed by this deposition technique. As it can be observed, the rod-shaped islands display an unusual arrangement along the highly symmetric directions of the substrates, in such a way that the predominant angles between them in a 100-substrates (figure 2a) are 90° and 30°, in contrast, in the 111-substrates are 60° (figure 2b). We are preparing a manuscript in which those tendencies are studied in more detail, but we assert in advance that the island density and growth mode are strongly affected by T_S.
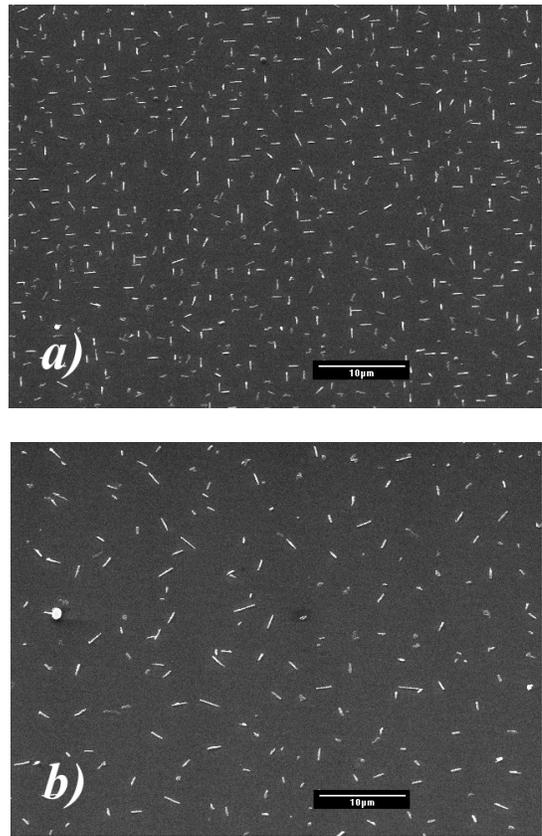
Fig. 2. – SEM micrographs displaying the unusual rod-shaped-island aligning on (111)-Si (*a*) and (100)-Si (*b*).

Figure 3 shows the x- ray diffraction peaks for films deposited on (111) and (100) silicon substrates at P_N = *25 mTorr* and T_S =*750°C*. As it can be distinguish in figure, exist diffraction at *38.16^o* from films deposited in both substrates, yielding an interplanar spacing of *2.35 Å*. This distance matches the (222)-α-Be_3N_2 interplanar spacing [6]. One remarkable result is that the films grow preferentially in the [111] direction, independently of the substrate orientation.

The figure 4 is a TEM cross section of the film deposited on a (111)-*Si* substrate. The axis zone for *Si* is [110]; were we distinguish a set plane with a spacing of *3.1Å*, in harmony with silicon's {111} interplanar spacing. Over the substrate, as it can be noticed in figure 4, exist a well-arranged crystalline film. Using the interplanar distance of silicon as a calibration reference, the film's interplanar distance can be estimated in a *2.1Å*, at an angle of *71°*, matching the {210} family of the α-*Be$_3$N$_2$*. The orientation relation film/substrate is then [110]// [$2\bar{1}0$] and ($1\bar{1}1$)//($\bar{1}\bar{2}3$). One intriguing result from TEM cross-section is that we do not observe the native *SiO$_2$* layer.
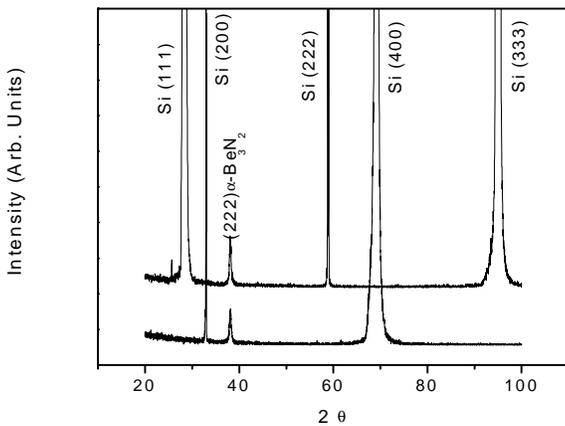
Fig. 3.- XRD spectra of the α-Be$_3$N$_2$ films growth on *a*) (100)-Si and *b*) (111)-Si
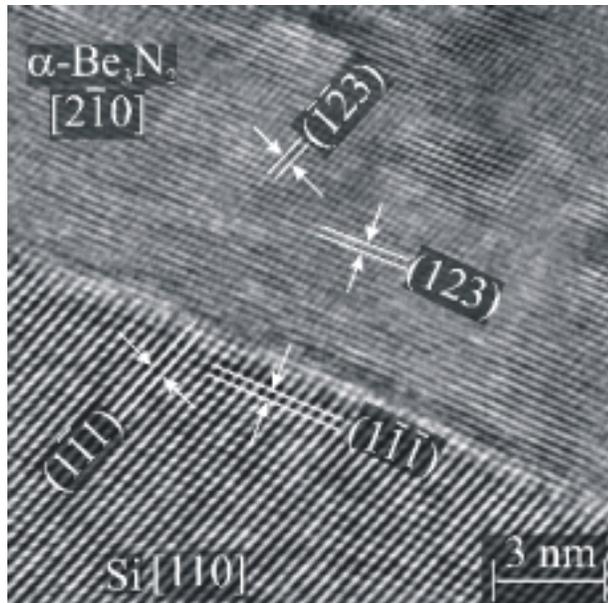
Fig. 4.- HRTEM cross-section of a α-Be$_3$N$_2$ film deposited on (111)-Si.

Since our preparation temperatures were not high enough to remove this oxide before deposition, we assume that the oxygen atoms have migrated from *SiO$_2$* to the film. To corroborate this supposition we made several *ex-situ* auger depth profiles. Figure 5 illustrates a typical result, where the normalized peak-to-peak intensities for each constituent element are show. The exposure to air causes the creation of an oxidized *BeN$_x$O$_y$* surface layer; past this thin layer the composition of the film is homogeneous. The film/substrate interface is abrupt, in consistency with TEM data, as is revealed by the rapid decrease of *Be* and *N* and the increase of *Si* signals. However near the interfacial region the oxygen signal comes out in advance of the silicon signal, as if it originated from the films instead as of the substrate. Since the oxygen incorporation during the growth process can be ruled out, we suppose that oxygen diffused form the native silicon dioxide layer to the oxygen greedy beryllium, producing the manifestation of the *BeN$_x$O$_y$* interfacial layer, however in depth analyses is needed to understand how the oxygen atoms incorporate in the *Be$_3$N$_2$* matrix and the role it plays in the film's epitaxy.
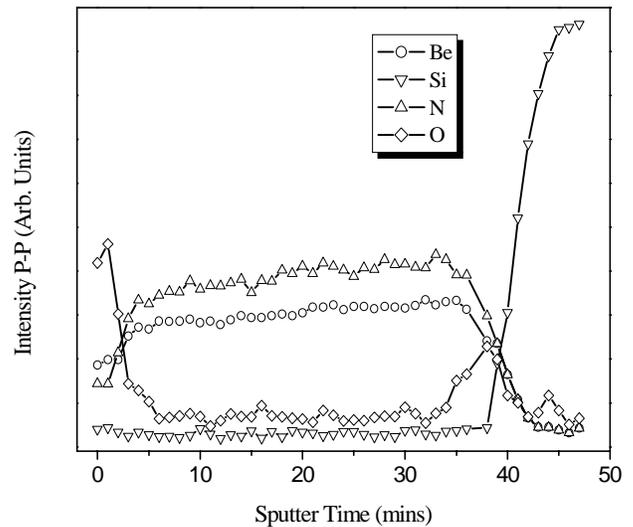
Fig. 5.- Typical AES depth profiling of beryllium nitride film on silicon. As it should be peak-to-peak intensities are shown.

4. Conclusions

The epitaxy of beryllium nitride on silicon is effortlessly achievable at moderate high temperatures by ablating a beryllium foil in the presence of molecular nitrogen. The film grown in the "*alpha*" phase, with orientation relationships $[110]//[2\bar{1}0]$ and $(1\bar{1}1)//(\bar{1}\bar{2}3)$ on (111)-*Si*. The oxygen diffuses from the native SiO_2 layer toward the film, producing a buffer BeN_xO_y interfacial layer. We hope that these results encourage the research of the direct-band-gap beryllium nitride as a viable candidate to be implemented in optoelectronic devices.

Acknowledgments

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