Vol 18 No 3, March 2009
1674-1056/2009/18(03)/1266-04
Chinese Physics B
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Effect of growth temperature on morphology, structure and luminescence of Tb-doped BN thin films*

Liu Quan-Lin(刘泉林)[a)b)†], Yu Guang-Hua(于广华)[a)], and Jiang Yong (姜 勇)[a)]

[a)] *State Key Laboratory for Advanced Metals and Materials, School of Materials Science & Engineering, University of Science and Technology Beijing, Beijing* 100083, *China*
[b)] *Advanced Materials Laboratory, National Institute for Materials Science, Namiki* 1-1, *Tsukuba, Ibaraki* 305-0044, *Japan*

(Received 25 July 2008; revised manuscript received 18 August 2008)

This paper investigates the effect of growth temperature on morphology, structure and photoluminescence (PL) of Tb-doped boron nitride (BN) films grown by magnetron sputtering, and the relationships of growth-temperature-structure-PL by scanning electron microscopy, transmission electron microscopy and PL. The characteristic emission lines of the Tb^{3+} were observed in the PL spectra at room temperature. The 473-K-grown film is mainly consisted of amorphous BN particles. With the growth temperature increasing up to 1273 K, the amount of amorphous BN decreases, while the amount of turbostratic BN increases. Correspondingly, the PL intensities from the Tb^{3+} ions increase with the increase of temperature in the range of 473–1273 K.

Keywords: boron nitride, rare earth doped, photoluminescence, thin film growth
PACC: 7855D, 8115N, 6116D

1. Introduction

Rare-earth (RE)-doped wide-band-gap semiconductors have attracted considerable interest in recent years owing to the attempt to develop novel optoelectronic devices, which combine the electronic properties of semiconductors with the unique luminescence features of RE ions.[1] The light emission involved in the intra-4f transitions of trivalent RE ions is sharp and well-defined because the 4f shell is shielded from its surroundings by the filled 5s and 5p shells. A significant amount of work has been reported on the study of visible emissions from RE-doped GaN[2−5] and AlN.[6−9] Boron nitride (BN) exhibits a wide band gap of around 5.2 eV and many advantages including thermal and chemical stability, low density, and high thermal conductivity. In our previous work,[10,11] we reported red, green and blue emission from N-rich turbostratic BN thin films doped with Eu, Tb, and Tm, respectively, which were grown on silicon substrate by radio-frequency (RF) magnetron sputtering. Magnetron sputtering technique is a low-cost, large-area, and easy-control method for film growth. In the present work, the Tb-doped BN films have been grown by magnetron sputtering at various substrate temperatures from room temperature (RT) to 1673 K. Here we report the effect of growth temperature on morphology, structure and photoluminescence (PL) of Tb-doped BN films, and the relationships of growth-temperature-structure-PL.

2. Experimental

The Tb-doped BN films were deposited by RF magnetron sputtering using a water-cooled 50-mm diameter TbB_6 target in argon/nitrogen mixtures. The deposition chamber was pumped down to less than 2.0×10^{-4} Pa. The distance of target to substrate is about 80 mm. Sputtering was conducted in N_2/Ar mixtures under a pressure of 0.8 Pa (partial pressure of N_2 is about 0.4 Pa) and a RF-discharge power of 100 W. The films were grown on silicon (100) substrates at various temperatures from RT to 1273 K and on SiC substrates at 1673 K. The substrates were cleaned by dipping the substrates in a diluted HF solution (H_2O : HF (49%) = 30 : 1) for 10 minutes at RT, and then treated by organic solvents. All samples had been grown for about 2 hours. The morphology and structure of the films were investigated by means

*Project supported by the National Natural Science Foundation of China (Grant No 50672007), the NCET-06-0082, and the MOST 973 Program of China (Grant No 2007CB936202).
†E-mail: qlliu@mater.ustb.edu.cn

of: scanning electron microscope (SEM), infrared (IR) absorption, transmission electron microscope (TEM). The PL spectra were measured at RT by using a He–Cd laser as the excitation source with a wavelength $\lambda_{exc} = 325\,\text{nm}$.

3. Results and discussion

Figure 1 shows the surface morphology of the films deposited at about 473, 873, 1073 and 1273 K, respectively. When the substrate temperature is about 473 K, the surface shows grain growth, with the grain size of about 50–100 nm (Fig.1(a)). When the substrate temperature is increased to 873 K, the size of grain is reduced to about 20–50 nm, and film turns more solid and smooth (Fig.1(b)). With further increase of the substrate temperature, the grains turn smaller and their boundaries turn blurry (Figs.1(c) and 1(d)). The above results show that with increasing substrate temperature, the grains are more fused with surrounding grains. With the increase of growth temperature, the Tb dopants can be more equably distributed in the films during fusing, which may be accounted for the increase of PL intensity.

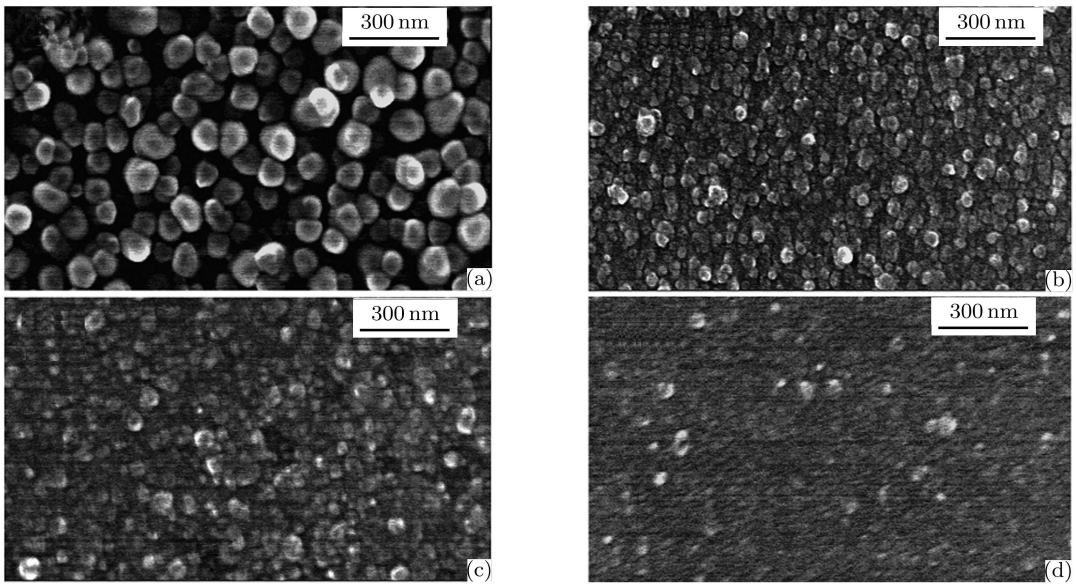


Fig.1. The SEM images of the films deposited at about 473 (a), 873 (b), 1073 (c) and 1273 K (d), respectively.

Figure 2 shows the IR spectra of the films grown at 473, 873, 1273 K, respectively. All films exhibit the typical IR bands of hexagonal BN (h-BN), i.e. a strong absorption band at $\sim$1386 cm^{-1} and a weaker band at $\sim$784 cm^{-1}. These bands are attributed to the in-plane B–N stretching mode of vibration and the out-of-plane B–N–B bending vibration mode. The characteristic absorption band of cubic BN, i.e. at 1100 cm^{-1}, is not obviously observed, indicating the absence of the c-BN phase. The IR spectra of the films grown at different temperatures are very similar to each other.

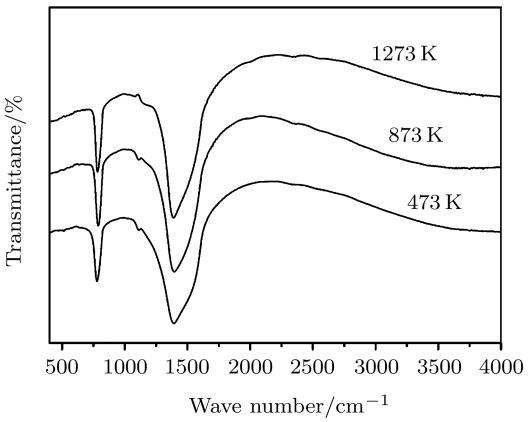


Fig.2. The IR spectra of the films grown at 473, 873, 1273 K, respectively. For clarity the IR spectra of 873- and 1273-K-grown films were shifted upwards.

The structural details of the films deposited at various temperatures were further investigated by high-resolution transmission electron microscopy (HRTEM) as shown in Fig.3. Selected-area electron diffractions indicate that BN has two structures, i.e. amorphous BN and turbostratic BN. A turbostratic phase has a partially ordered, pseudographitic form,

which is a layer-structure with a rotational disorder in the direction normal to the layer.[12] The three innermost diffuse rings refer to the (002) reflection at ∼0.356 nm, the (10) reflection (unresolved (100) and (101) reflections for hexagonal BN) at ∼0.214 nm, and the (110) reflection at ∼0.126 nm, respectively. The HRTEM and SEM images show that the particles in 473-K-grown films are mainly amorphous BN. With increasing growth temperature up to 1273 K, the amount of amorphous BN particles decreases, while the amount of turbostratic BN increases. The turbostratic BN crystallizes more perfectly with the increase of growth temperature (the diffraction rings turn clearer and sharper). When growth temperature is up to 1673 K, another phase (or more phases) is formed (more diffraction spots appear as shown in Fig.3(d)). However, its structure is unknown, further investigations are in progress.

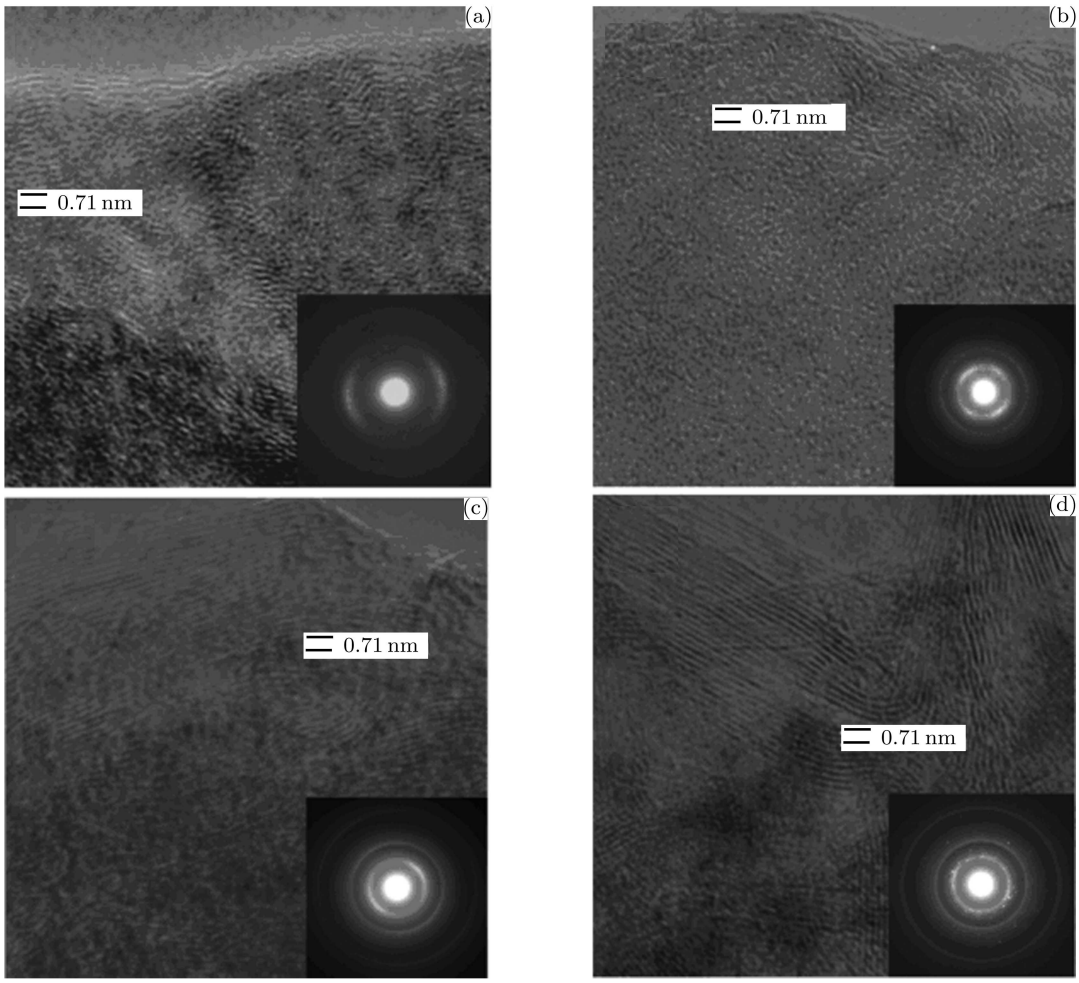


Fig.3. The Electron diffraction patterns and the corresponding high-resolution TEM images of Tb-doped BN films grown at 473 K (a), 873 K (b), 1273 K (c), and 1673 K (d), respectively.

The Tb content was studied by electron probe microanalysis (EPMA). TbP_5O_{14} compound was used as standard samples to calculate the content of Tb. The EPMA results give a composition in atomic percent of ∼2.9% for Tb. Figure 4 shows the PL spectra of the films deposited at the different substrate temperatures. All the PL spectra were recorded at the same conditions and, therefore, the relative intensities are directly comparable. The PL spectral features of various films are almost same, although the PL intensities vary largely. The PL peak at ∼544 nm is strongest in the investigated range, indicating that the film has strong green light emission. The intense green emission of the film by He–Cd PL excitation (at 325 nm) is visible with the naked eye. The strongest emission peak corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ions. Other PL peaks have been identified and correspond to the following transitions: $^5D_4 \rightarrow {}^7F_5$

(at ∼544 and 554 nm), $^5D_4 \rightarrow {}^7F_6$ (at ∼489 nm), $^5D_4 \rightarrow {}^7F_4$ (at ∼594 nm), $^5D_4 \rightarrow {}^7F_3$ (at ∼625 nm), $^5D_4 \rightarrow {}^7F_2$ (at ∼655 nm) and $^5D_4 \rightarrow {}^7F_{1,0}$ (at ∼689 nm).

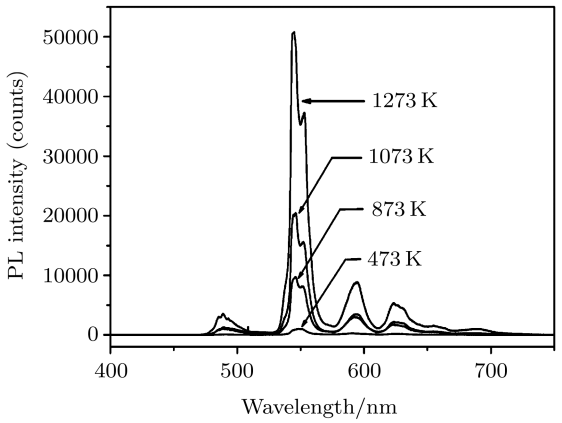


Fig.4. The PL spectra of the films deposited at the different substrate temperatures.

As shown in Fig.4, the PL intensities increase drastically with the increase of the substrate temperature from 473 K to 1273 K. However, the PL intensities for 1673-K-grown films are lower than those for 1273-K-grown films (here not shown). The dependence of PL intensity on the substrate temperature can be explained by the dependence of film structure on the growth temperature. Our experimental results show that the growth temperature has important effects on the morphology, structure and luminescent properties. In the deposit film process by sputtering, most of the flux arrives at the substrate surface in atomic form with energies ranging from 10–40 eV. These ad-atoms diffuse around the substrate and their diffusivities are dependent on the temperature of the substrate and the interaction between the ad-atoms and the substrate. At lower temperature, these ad-atoms diffuse difficultly, resulting in amorphous phase. At higher temperature, these ad-atoms can diffuse, leading to a turbostratic phase. Because high temperature can enhance ad-atom mobility, Tb atoms can keep moving around and finally arrive at equilibrium sites. Thus, activation of the Tb^{3+} ions can be enhanced, and it leads to enhancement of PL of the films. When temperature is up to 1673 K, Tb atoms can be congregated due to diffusion and formed another phase, it results in the decrease of PL intensity due to the concentration quenching. These results show that the optimum growth temperature is about 1273 K.

In summary, the Tb-doped BN thin films were grown by magnetron sputtering with various substrate temperature. With the increase of growth temperature, the amount of amorphous BN decreases, while the amount of turbostratic BN increases. The PL intensities from the Tb^{3+} ions increase with the increase of temperature in the range of 473–1273 K.

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