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High-temperature diffusion of the acceptor impurity Be in AlN

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The high-temperature diffusion of an acceptor impurity of beryllium (Be) into bulk single-crystal aluminum nitride (AlN) has been studied. It is shown that the introduction of Be leads to the appearance of green luminescence of AlN, which is stable at room temperature and is observed over the entire thickness of the sample. It was shown by the method of luminescence analysis that the Be diffusion process is most efficiently realized in the temperature range from 1800 to 2100°C and is characterized by extremely high diffusion coefficients $D = 10^{-7}\,\text{cm}^2/\text{s}$ and $10^{-6}\,\text{cm}^2/\text{s}$, respectively. It is shown that a prolonged diffusion process ($t \leq 1$ hour) at a temperature of 2100°C leads to concentration quenching of the luminescence of near-surface AlN layers with a thickness of $\approx 80\,\mu\text{m}$, which makes it possible to estimate the concentration of beryllium impurities in the near-surface layer on the order of $\sim 10^{19}\,\text{cm}^{-3}$.

Keywords: AlN PVT doping diffusion.

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1. Introduction

Currently, semiconductors from III-nitride (InN, GaN, AlN) family and combination of their solid solutions ($\text{Al}_x\text{Ga}_{1-x}\text{N}$, InGaN) form a basis for the development of an advanced photonics, power and high-frequency electronics framework [1]. Aluminum nitride (AlN) is a prominent representative of III-nitrides that is a direct-gap semiconductor with an extremely wide bandgap ($E_g \approx 6.1\,\text{eV}$) [2]. High E_g ($\approx 203\,\text{nm}$) allows to use this material for production of LEDs operated in middle (UV-B) and deep (UV-C) ultraviolet bands [1] and provide high critical breakdown field to ensure the benefits of AlN for production of power electronic devices [1].

The main problem to be solved to enable the use of AlN in the above mentioned areas includes provision of effective doping methods using *p*-type and n-type dopants that form shallow levels in the bandgap. Nominally undoped AlN is a *n*-type semiconductor [3], and the properties of *p*-type dopants such as silicon substituting aluminum atoms (SiAl) [4,5] and oxygen substituting nitrogen atoms (O_N) [6,7], have been investigated rather adequately. At the same time, as it was before and in case of GaN [8], there is much concern about the development of *p*-type conductivity AlN [3]. Similar to GaN, Mg in aluminum substitution position (AlN:Mg [9,10]) has been recognized as *p*-type dopant. Investigations of AlN:Mg crystal properties have shown that such crystals really have *p*-type conductivity, however, due to high activation energy of *p*-type dopants $E_a(\text{Mg}_\text{Al}) \approx 500\,\text{meV}$ [9,10], achievement of efficient *p*-type conductivity in such system is challenging task, in other words, AlN:Mg has a high resistivity $\sim 10^8\,\text{Ohm}\cdot\text{cm}$ [11]. However, alternative *p*-type dopants include impurities for Al substitution with II group chemical elements such as lithium (Li) and beryllium (Be). Thus, several experimental investigations of Be impurity in AlN suggested that Be_Al was an ideal *p*-type dopant with activation energy $\sim 223-340\,\text{meV}$ [12,13]. We have previously shown that introduction of Be atoms into bulk single-crystal AlN by means of high-temperature vapor diffusion results in drastic changes in AlN properties such as optical absorption suppression in visible and ultraviolet bands and significant displacement of Fermi level position towards the valance band ceiling to ensure identification of Be_Al impurity as a *p*-type dopant and demonstration of high AlN doping performance by high-temperature diffusion [14,15]. Investigations of electrophysical properties of Be-doped AlN during growth by metal-modulation epitaxy (MME) method have shown unique properties of Be as a *p*-type dopant. In particular, *p*-type conductivity of these crystals has been demonstrated, *p*-type dopant activation energy $E_a(\text{Be}_\text{Al}) \approx 37\,\text{meV}$ [16] has been found to be more that an order of magnitude lower than $E_a(\text{Mg}_\text{Al})$ [9,10]. Thus, the investigation of Be-doped AlN crystals and properties of this impurity are of great interest.

This research included the investigation of the properties of AlN single crystals grown by high-temperature vapor sublimation (physical vapor transport (PVT)) [17,18] and beryllium doped by means of high-temperature vapor diffusion, with crystal luminescent profile recoding before and after diffusion. Taking into account a small size of Be^{+2} (0.4 Å) ion, that is smaller than tetrahedral and octahedral void sizes in AlN, high probability of Be diffusion into AlN at interstices shall be expected. Such mechanism is implemented, in particular, in Be diffusion into SiC [19] that is very close to AlN in terms of the nature of chemical bond and binding energy.

2. Experimental part

Beryllium diffusion into single-crystal AlN samples grown by sublimation method has been examined [17]. For this, plates with a thickness from 0.3 to 1.5 mm were cut from ingots and then ground and polished. The samples were amber and had dislocation density from $5 \cdot 10^{-4}$ to $2 \cdot 10^{-5}\,\mathrm{cm}^{-2}$.

Be diffusing was carried out from tantalum carbide in nitrogen atmosphere in a closed vessel. High purity metallic Be was used as a diffusant that was placed in a boron nitride crucible. The test samples were placed on a BeN plate in an area with the minimum temperature gradient. The diffusion temperature varied from 1700 to 2100°C, annealing period was 0.5−10 h. It shall be noted that the sample evaporation during the diffusion annealing period was negligible.

Before Be diffusion, the test samples were annealed in the same conditions. No changes in the material properties were observed during this process.

3. Results and discussion

Changes in optical absorption and photoluminescence of samples as a result of diffusion introduction of Be impurity have been studied herein.

After diffusion annealing in Be vapors at > 1700°C, dramatic reduction of crystal color intensity was observed. At moderate annealing temperatures (1600−1800°C), amber crystals became almost colorless (Fig. 1, *a, b*). However, an increase in the diffusion temperature > 2000°C made the crystals to acquire a dark-greyish tint whose intensity was growing with temperature and annealing time.

Photoluminescence intensity was measured using MLD-1 microscope with luminescence intensity and color recording. It was found that, after diffusion at < 2000°C, photoluminescence color was changed from yellowish to greenish (Fig. 2, *a, b*) at 300 K. Thus, the presence of green photoluminescence is an evident sign of Be introduction to a certain sample depth.

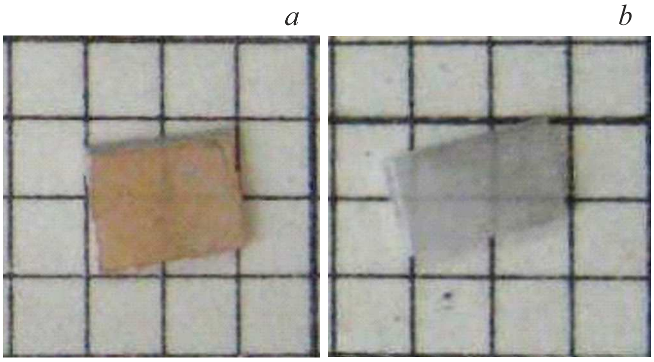

Figure 1. Painting of two AIN samples: *a* — reference standards, *b* — after Be diffusion, $T_{\mathrm{dif}} = 1860$°C, 2 h. (Colored figure is available in the electronic version of the article)

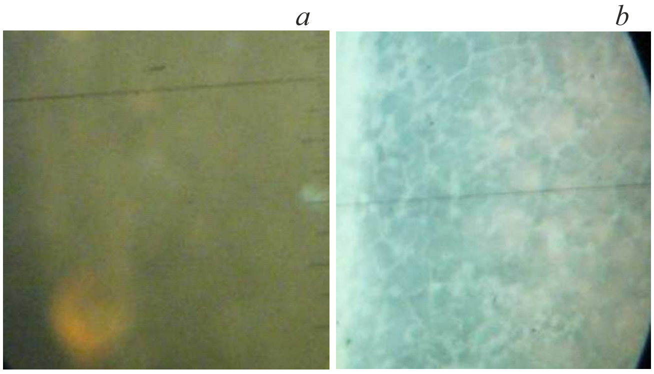

Figure 2. AlN sample luminescence at 300 K: *a* — reference standard, *b* — after Be diffusion, $T_{\mathrm{dif}} = 1860$°C, 2 h.

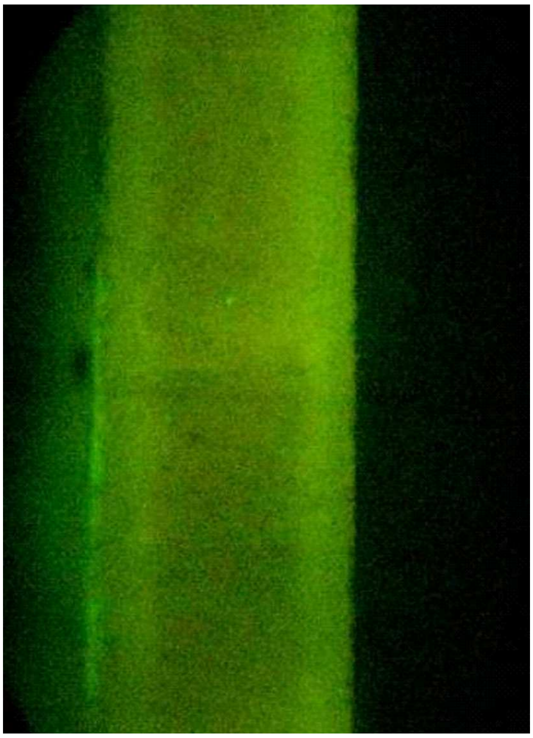

Figure 3. Luminescence of the sample end at 300 K after Be diffusion, 1860°C, 2 h. A surface layer with 100 μm bright green luminescence can be seen.

The difference in luminescence color of the initial crystal and diffusion layer allowed to assess Be diffusion. For this, thin sections were made on the crystal ends to measure the diffusion depth (Fig. 3). It can be seen that at 1850°C the green PL layer thickness was ~ 0.1 mm. According to this data, diffusion coefficient of Be in AlN may be assessed.

We use the equation describing impurity concentration distribution during diffusion from a constant source [18] $N(x,t) = N_0 \operatorname{erfc} x/2(Dt)^{0.5}$, where N_0 is a surface concentration, $N(x,t)$ is a diffusant impurity concentration depend-

Figure 4. Photo of the sample end luminescence at 300 K after Be diffusion, 2100°C, 2 h. A 80 μm dark near-surface layer can be seen. Sample thickness is 1700 μm.

ing on the depth and time, D is a diffusion coefficient, x is a diffusion depth, t is a diffusion time. The assessment shows that, at $N(x,t)/N_0 = 10^{-2}$, diffusion coefficient of Be with a standard diffusion profile is 10^{-7} cm^2/s. At higher temperatures, green luminescence typical of the diffusion layer is extended to the entire sample thickness. In addition, a near-surface negligibly luminescent layer was observed (Fig. 4). The observed dramatic reduction of luminescence quenching efficiency in near-surface layers may be explained by a concentration quenching effect and occurs at luminescence center concentration $n \geq 10^{19}$ cm^{-3}.

It shall be noted that the standard diffusion profile is not often observed. For example, Be diffusion in SiC is described by a more complicated profile that includes a steep near-surface and more smooth bulk regions [19]. It is evident that, similar to SiC, Be diffusion in AlN takes place at interstices with partial deposition in lattice points. High mobility of Be in AlN is facilitated by a small size of Be^{+2} ion (ionic radius is 0.41 Å). This conclusion can be made on the basis of high mobility of diffusing Be atoms that enables doping of AlN plates with a thickness of a few mm using this impurity.

4. Conclusion

Thus, the findings demonstrate that Be introduced by diffusion is very soluble in AlN, which makes it a promising material for production of conducting layers with p-type conductivity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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