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Citation: J B Xia, Efficient p-type doping in ultra-wide band-gap nitrides using non-equilibrium doping method[J]. *J. Semicond.*, 2021, 42(6).

View online: <https://doi.org/10.1088/1674-4926/42/6/060402>

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# Efficient p-type doping in ultra-wide band-gap nitrides using non-equilibrium doping method

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**Citation:** J B Xia, Efficient p-type doping in ultra-wide band-gap nitrides using non-equilibrium doping method[J]. *J. Semicond.*, 2021, 42(6), 060402. <http://doi.org/10.1088/1674-4926/42/6/060402>

Al-rich nitride, as one of the most important ultra-wide band-gap (UWBG) semiconductors, currently plays the key role of deep ultraviolet (DUV) optoelectronics and potentially possesses the advantages of the huge global investment in the manufacturing infrastructure associated with InGaN material that has become the second most important semiconductor material after Si in the late 2010s<sup>[1, 2]</sup>. However, the p-doping of Al-rich nitrides has long been blocking the improvement of quantum efficiency of DUV optoelectronics. The activation energy ( $E_a$ ) of the most-frequently used acceptor dopant Mg increases from 200 meV in GaN to as high as 630 meV in AlN<sup>[3–5]</sup>. Once the p-doping problem of Al-rich nitrides is solved, the DUV or even the high-frequency and high-power industries probably usher in an era of rapid development based on the existing manufacturing infrastructure.

Actually, most wide band-gap (WBG) semiconductors usually experience an asymmetry doping problem, i.e., they can only be easily doped n-type or p-type, while not both, which is because that they either have a low valence band maximum (VBM) or a high conduction band minimum (CBM), resulting extremely high acceptor or donor  $E_a$ <sup>[6, 7]</sup>. And for UWBG semiconductors, the problem gets even worse. For example, the  $E_a$  of N-doped or P-doped n-type diamond is generally higher than 0.5 eV and that of Mg-doped or N-doped p-type  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is even higher than 1 eV<sup>[8–10]</sup>. These doping asymmetry problems have seriously hindered the potential applications of many WBG materials.

In the past decades, great efforts have been devoted to theoretically overcome the high  $E_a$  problem in WBG semiconductors. In these investigations, researchers tried their best to develop novel approaches to tune the dopant level. For n-type doping, to lift the impurity level up close to the CBM of the host, while for p-type doping, to lower the impurity level down close to the VBM of host. The generally used dopant delta-doping and co-doping in WBG semiconductors are all based on the principle<sup>[11, 12]</sup>. Later, Yanfa Yan *et al.* proposed an approach to solve the asymmetry doping problem by introducing impurity band below the CBM or above the VBM via passive donor–acceptor complexes or isovalent impurities and effectively doping the passivated impurity band, which essentially changed the band edge<sup>[13]</sup>. Clas Persson *et al.* found the S dopants in ZnO would form local ZnS like bonds in the ZnO host and could result in a strong VB offset bowing, making the p-doping of ZnO enhanced<sup>[14]</sup>. From this point of

view, it is possible to reduce the  $E_a$  by tuning the band edge. However, it is difficult and uncontrollable to form such impurity band or local bonds as the authors declared.

Recently, Prof. Dabing Li's group in Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences (CAS), cooperating with Prof. Hui-Xiong Deng in Institute of Semiconductors, CAS, reported an interesting work in p-doping of Al-rich nitrides<sup>[15]</sup>. They proposed a non-equilibrium doping model to achieve low acceptor  $E_a$  in Al-rich nitrides, in which GaN quantum dots (QDs) are buried in AlN host to lift the VBM up, the Mg dopants are doped at the AlN host, and the Mg dopants are concentrated near the interface between GaN QDs and AlN host, as shown in Figs. 1(a)–1(c). In their model, Mg acceptor  $E_a$  below 0.1 eV is achieved according to the first principles calculations. Based on the model, p-type Al-rich AlGaN materials with Al contents of 50%–70% are experimentally realized. The hole concentrations reach the magnitude of  $10^{18}$  cm<sup>−3</sup> at room temperature and the measured acceptor  $E_a$  is several tens of meV as expected. The turn-on voltage of the DUV light-emission diode (LED) based on the non-equilibrium doping method is reduced compared to that based on the uniform doping method, as shown in Fig. 1(d). It is an exciting result for Al-rich nitrides.

This work is an important progress in WBG semiconductor doping. It has strongly developed the non-equilibrium doping process that to lower the dopant  $E_a$  by tuning the band edge of the host. Besides, it has found a good method to bury narrow band-gap QDs in their wide band-gap congener host, which will not significantly affect the optical properties of the host and is feasible in many element and compound semiconductors. It seems more controllable and designable compared to the formation of impurity band or local bonds. Moreover, it also demonstrates that not only the dopants formed based on non-equilibrium techniques like the dopant delta-doping, but also controlled growth of host materials based on non-equilibrium technology can power up the doping efficiency of WBG semiconductors. Therefore, this work has developed the doping conception that to lower the  $E_a$  of WBG semiconductors by tuning the band edge using non-equilibrium doping method. The follow-up studies should be carried out soon, breaking new frontiers in the doping of WBG and UWBG semiconductors.

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Received 30 APRIL 2021.

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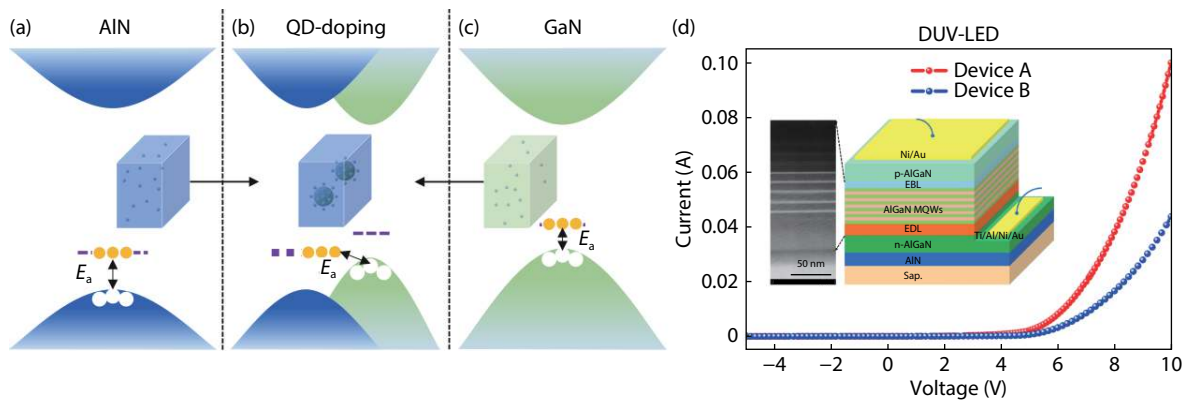


Fig. 1. (Color online) Non-equilibrium doping method to lower the acceptor  $E_a$  in UWBG nitride semiconductors and its application in DUV-LED. Acceptors are randomly doped in (a) AIN and (c) GaN. Both have high  $E_a$  in this condition. (b) GaN-QDs are embedded in AIN host and acceptors are doped in AIN host and concentrate near the interface. (d) Current-voltage curves of the devices. Device A uses the non-equilibrium doping method and Device B uses the uniform doping method. The insets are the device structure diagram and the cross-sectional scanning transmission electronic microscopy for the active region of the devices. Cited from Ref. [15].

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