Thermal degradation of InGaN quantum wells - in-situ TEM studies

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Active parts of green nitride laser diodes consist of InGaN quantum wells (QWs) with In content higher than 25%. It is observed that such layers are thermally unstable and tend to degrade, especially when they are overgrown by layers doped with Mg, which require about 250°C higher growth temperatures than the growth temperature of InGaN QW (Fig. 1). The degraded areas of QW consist of voids overgrown by thin layer of almost pure InN and filled with crystalline In and some amorphous material. The sizes of these features exceed the width of the degraded QW and the range of thermally degraded areas is laterally growing with time of annealing. In the TEM studies, we also observe areas, where the QWs are still present, but contain smaller voids situated at the lower interface of the QW (Fig. 1(c)). These voids are possibly formed at the first stages of degradation, where diffusion of metal atoms takes place, what is most probably realized by the diffusion through vacancies. Such a diffusion mechanism may lead to agglomeration of vacancies and formation of the observed voids. The surfaces of the voids are the places, where the bonds between nitrogen and metal atoms may break, as it is observed in the case of the annealing of the InGaN layer's surface, which is easily etched when exposed to a temperature higher than 800˚C. Metal atoms and nitrogen atoms then probably gather inside such a growing void. When cooling takes place, the phase with higher crystallization temperature is formed first - in this case GaN. At lower temperature the crystallization of InN takes place (Fig. 1 (d)), the residues of the melted material stay inside the void in the form of metallic inclusions of indium and possibly gallium, which should remain liquid at the room temperature.

In order to study the thermal degradation process and to confirm that the formation of voids is the first stage of this phenomenon, we carried out in-situ annealing experiments of the structures containing InGaN QWs. This studies were performed with a FEI Titan 80-300 microscope equipped with a Protochips Atmosphere holder for in-situ heating experiments in a gas cell. The first stages of thermal degradation were observed at the temperature of 800˚C (Fig.2(b)). Then we annealed the sample at this temperature for 30 minutes. During this annealing, we observed that in the limited area of the specimen, all quantum wells were decomposing by formation of voids. The voids were growing in the lateral direction of QWs and droplets of liquid metal inside them were observed (FIG. 2(c)). When we lowered the temperature to 500˚C, we observed formation of high In-content layers at the bottom of voids. We performed these experiments in the protective atmosphere of gaseous nitrogen and also in vacuum. The degradation process took place very rapidly in these in-situ experiments, what could be due to limited volume of quantum wells inside TEM specimen and due to the vicinity of specimen surfaces, which definitely changed the mechanism of the diffusion processes inside the QWs.

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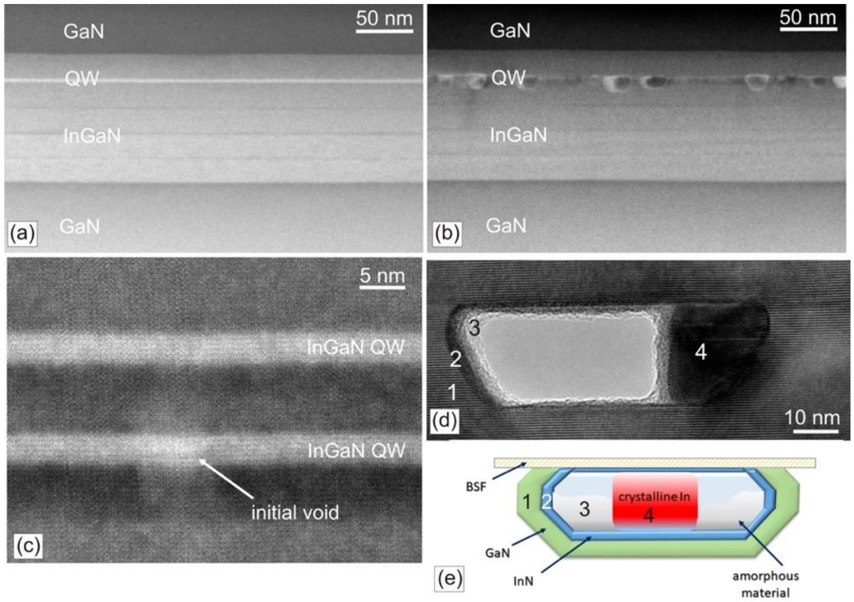

Fig. 1. STEM images of the structure with InGaN QW (a) as grown; (b) after annealing in the growth reactor for 1h at 950 ˚C in ammonia; (c) image of an initial void present in the lower QW; (d) voids overgrown by InN and partly filled with metallic In inclusion; (e) schematic representation of phases observed after the recrystallization of the decomposed QW area.

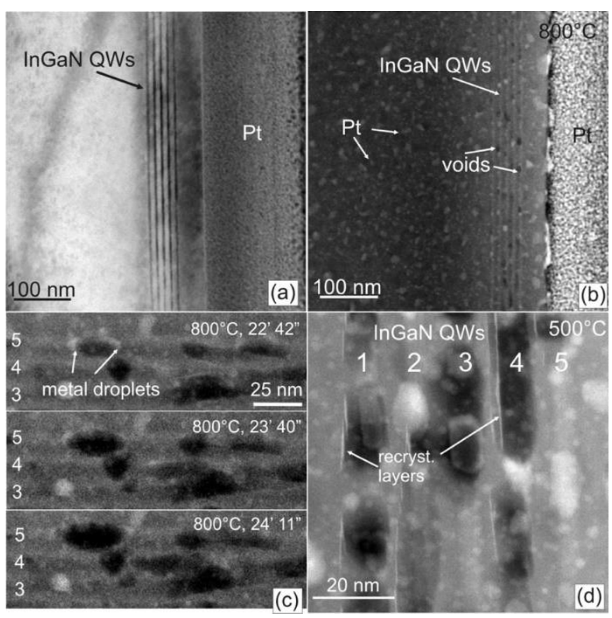

Fig. 2 (a) Bright field TEM image of the structure with InGaN QWs before the in-situ annealing; (b) STEM image of the same area as in (a) at the first stage of thermal degradation observed at 800˚C; contamination by Pt occurred during last stages of FIB specimen preparation (c) STEM images showing the evolution of voids sizes with the increasing time of the annealing (d) STEM image of the QWs after annealing at 800˚C for 30 min and cooled down to 500˚C, the recrystallized layers with high In content formed at the bottom of voids are marked with arrows.