Effects of polarization and p-type GaN resistivity on the spectral response of InGaN/GaN multiple quantum well solar cells*

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Effects of polarization and p-type GaN resistivity on the spectral response of InGaN/GaN multiple quantum well (MQW) solar cells are investigated. It is found that due to the reduction of piezoelectric polarization and the enhancement of tunneling transport of photo-generated carriers in MQWs, the external quantum efficiency (EQE) of the solar cells increases in a low energy spectral range ($\lambda > 370$ nm) when the barrier thickness value decreases from 15 nm to 7.5 nm. But the EQE decreases abruptly when the barrier thickness value decreases down to 3.75 nm. The reasons for these experimental results are analyzed. We are aware that the reduction of depletion width in MQW region, caused by the high resistivity of the p-type GaN layer may be the main reason for the abnormally low EQE value at long wavelengths ($\lambda > 370$ nm).

Keywords: nitride materials, external quantum efficiency, polarization, p-type GaN resistivity

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1. Introduction

The excellent material properties which make III–N semiconductors attractive for light-emitting diodes[1] are advantageous for high performance solar cells. The most unique property is the tunable band gap ranging from 0.7 eV for InN[2] to 3.4 eV for GaN, which can cover most of the solar spectrum. In addition, the properties of high mobility of carriers, high resistance against irradiation damage, and high absorption coefficients ($\sim 10^5$ cm^{-1})[3] also present a great potential for photovoltaic applications. However, the growth of InGaN alloy with both high indium content and high quality, which is essential for high efficiency InGaN solar cells, suffers great challenges.[4] According to previous research, in order to obtain a high crystal quality InGaN absorption layer suitable for conventional p-GaN/i–InGaN/n–GaN solar cells, the In content of the InGaN layer must be less than 15%. In this case, the conversion efficiency of p-GaN/i–InGaN/n–GaN solar cells is less than 1%.[5,6] To improve conversion efficiency of InGaN solar cells, new growth methods or structure need to be explored.

Recently, the multiple quantum wells (MQWs) or superlattices have been employed in InGaN solar cell structures.[7,8] In the MQWs, the InGaN quantum well layers are thin enough to stay below the critical thickness value and allow high In content compared with thicker InGaN layers. In addition, the high growth temperature of quantum barrier layers can remarkably improve the crystal quality of MQW absorption layer.[9] So the InGaN/GaN MQW solar cells may exhibit higher conversion efficiency (close to 3% under AM 1.5 G illumination).[7] However, their performance is still not as high as expected. We should investigate the properties of InGaN MQW solar cells in depth and find methods to improve the performance of solar cells.

In this paper, the spectral responses of InGaN/GaN multiple quantum well (MQW) solar cells with different barrier thickness values are investigated, and the influences of polarization effect and the resistivity of p-type GaN on external quantum efficiency (EQE) are analyzed in detail, which may provide a substantial base for the research of super-high efficiency solar cells. In this work, the theoretical analyses for the electric field distribution and energy band of solar cells are made using APSYS simulation program. The $In_{0.3}Ga_{0.7}N$/GaN MQW solar cells are grown by metal–organic chemical vapor deposition (MOCVD), the data of EQE testing are presented and analyzed. The structural properties of the solar cells are characterized by X-ray diffraction (XRD), electroluminescence (EL), photoluminescence (PL) and circular transmission line model (CTLM) *I*–*V* testing.

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2. Experiment

InGaN/GaN MQW solar cells were grown on c-plane sapphire substrate using MOCVD. Trimethylgallium, trimethylindium, and ammonia were used as Ga, In, and N precursors, respectively. The device structure of the solar cells consisted of a 3-μm Si-doped n-type GaN layer ($n = 3 \times 10^{18}$ cm^{-3}) grown at 1040 °C, 15 periods of unintentionally doped $In_{0.3}Ga_{0.7}N$/GaN MQWs, and a 130-nm Mg-doped p-type GaN layer grown at the low temperature of 960 °C. The thickness value of $In_{0.3}Ga_{0.7}N$ QW was fixed to be 3 nm, and the thickness values of the GaN barrier were 15, 7.5, and 3.75 nm per period, respectively, which were denoted as samples A, B, and C. Then the solar cell devices were processed into 1.2 mm×1.2 mm mesas through etching down to the n-type GaN by ion beam etching technique. The Ni/Au (5 nm/5 nm) semitransparent Ohmic contact layers were deposited on p-GaN layer by electron beam evaporation, followed by rapid thermal annealing at 500 °C in a forming gas of N_2:O_2 (2:1) for 5 min. Finally Ti/Al/Ti/Au (15 nm/250 nm/50 nm/250 nm) layers were deposited on both Ni/Au semitransparent film and n-type GaN to form p-type and n-type electrodes.

3. Results and discussion

As is well known, the piezoelectric polarization of InGaN layer can largely affect the collection of photo-generated carriers because it has large influences on electric field and energy band profile of the MQW region. In the GaN/InGaN MQW region, the total electric field is a vector sum of the built-in electric field and the polarization-induced electric field. The piezoelectric polarization-induced electric field has a direction opposite to the built-in electric field, thus when the effect of piezoelectric polarization decreases with the reduction of barrier thickness, the total electric field in the MQW region will increase. The barrier thickness value thus may have a large influence on the carrier collection of solar cells due to its effect on the total electric field of the MQW region.

In this work, the electric fields and energy bands of $In_{0.12}Ga_{0.88}N$/GaN MQW solar cells with different barrier layer thickness values (3 nm, 6 nm, 9 nm, 15 nm) are first investigated using APSYS simulation program. The results are shown in Fig. 1. It is found that the electric field in quantum well and barrier layers changes ascendingly with the reduction of the barrier thickness value, which results in an increased tilt (slope) of the energy band for the quantum barrier and a decreased tilt for the well. When the barrier thickness is sufficiently thin, the total electric field in the quantum well increases over zero value due to the reduction of piezoelectric polarization with barrier thickness value decreasing (the electric field induced by piezoelectric polarization becomes less than built-in electric field), and the tilt of energy band for the quantum well turns to an opposite direction; this barrier thickness can be called critical barrier thickness. (It is noted, however, that the variation of the tilt of the energy band is due to the lower piezoelectric polarization effect resulting from a lower In content of 12% in our simulated InGaN QW layer. When the In content is as high as 30% in the real solar cell sample, the piezoelectric polarization effect will monotonically increase with the increase of In content, which will result in a reduced critical barrier thickness). In this process, the potential barriers of carriers in both conduction band and valance band decrease with barrier thickness decreasing, which is helpful for the photo-generated holes (electrons) in the MQW region thermionic emitting over the quantum barrier layers to reach p-GaN (n-GaN) contact layer and result in an increase of the collection efficiency of solar cells.

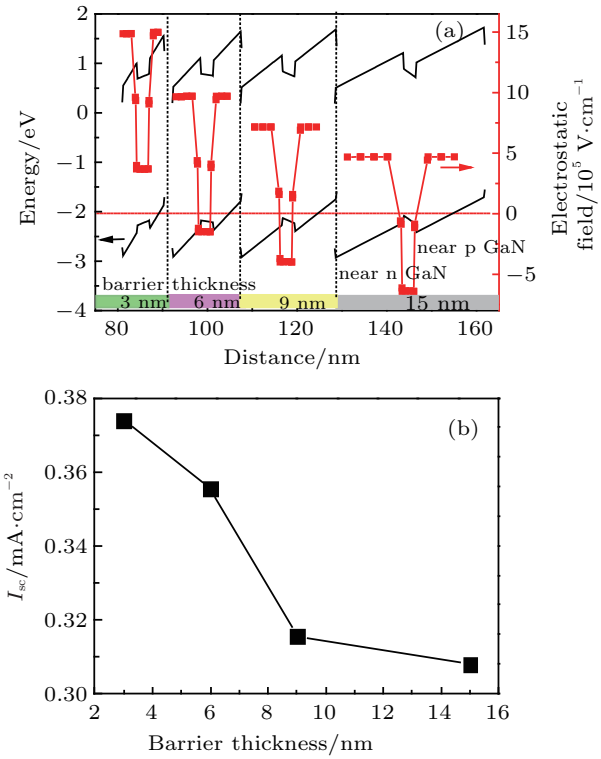


Fig. 1. (color online) (a) Energy band diagrams and the electric field of 4 single QWs with 3-nm InGaN well width. The GaN barrier thickness values are taken to be 3 nm, 6 nm, 9 nm, 15 nm, respectively. (b) Dependence of the short circuit current density on the barrier thickness.

On the other hand, the tunneling current may also play an important role in the MQW solar cells with high field and thin barrier layers.[10] The tunneling effect of photo-generated carriers may be enhanced due to the increase of electric field and the reduction of tunneling barrier width in the MQW region with barrier thickness value decreasing. Thus good collection efficiency of carriers for solar cells with a thin barrier thickness may be expected, while the mechanisms that allow photo-generated carriers to escape from the MQW region and contribute to the photo current are tunneling through or thermionic emitting over the quantum barrier layers. Thus the obtained spectral response increases with the reduction of

barrier thickness (as shown in Fig. 1(b)), showing clearly the effect which may be induced by changing piezoelectric polarization and tunneling effect in the MQW region.

Following the theoretical analyses for the spectral response of solar cells with different barrier thickness values, the EQEs of three GaN/InGaN MQW solar cells with different barrier layer thicknesses, 15, 7.5, and 3.5 nm, are measured. The devices are illuminated with an Xe lamp during the EQE (λ) measurement. The incident light power is measured by a calibrated silicon photodetector. As shown in Fig. 2, the EQE of sample B is lower than that of sample A and sample C when the wavelength is less than 370 nm, but when the wavelength is greater than 370 nm, its EQE is largest.

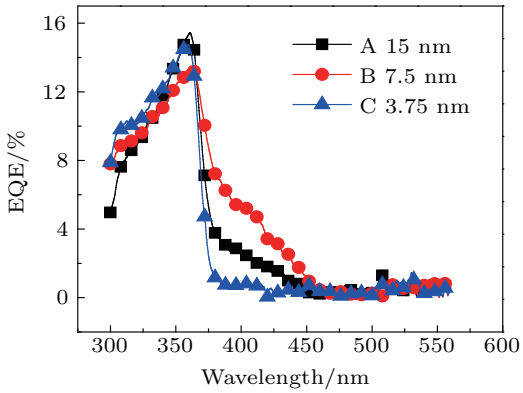


Fig. 2. (color online) Variations of external quantum efficiency with wavelength for samples A, B, and C at zero applied bias.

As is well known, the spectral response of a GaN/InGaN solar cell device at wavelength greater than 370 nm comes from the absorption of InGaN QWs, and the absorption of the incident light of wavelength less than 370 nm comes from the GaN layers, which include the p-type GaN layer and GaN quantum barrier (QB) layers. However, a 130-nm thick p-GaN layer may absorb nearly 80% of incident light due to the high absorption coefficients ($\sim 10^5$ cm^{-1}),[3,4] so the spectral response for the wavelength less than 370 nm in Fig. 2 mainly comes from the absorption of the p-type GaN layer. According to the above described theoretical analysis, when the barrier thickness decreases from 15 nm to 7.5 nm as shown by the curves of sample A and sample B, the observed increase of EQE at wavelength greater than 370 nm may result from the reduction of the piezoelectric polarization of MQWs and the enhancement of transport of photo-generated carriers in the MQW region. But it is found that the EQE decreases abruptly when the barrier thickness value decreases down to 3.75 nm (sample C). This phenomenon is just opposite to what is expected by the theoretical analysis mentioned above and therefore cannot be explained in a simple way. We think such an experimental result may be caused by the poor quality of InGaN QWs or the p-type GaN layer of sample C. As is well known, the Shockley–Read–Hall (SRH) recombination rate of the InGaN/GaN MQW with poor crystal quality of InGaN layer will increase, which may result in a weak spectral response on the low energy side ($\lambda > 370$ nm). In addition, the depletion width of the MQW region which is dependent on the n-type unintentionally doped concentration of the MQW layer and the effective p-doping concentration of the p-type GaN layer may also have a great influence on the spectral response of solar cells. If the background doping level is high, or the effective p doping concentration (hole concentration) of the p-type GaN layer is low, the depletion width of the MQW region will be reduced, and the carriers generated from a large number of InGaN QWs will be not able to be collected by the electrodes, resulting in a degraded spectral response even though the piezoelectric polarization of MQWs decreases when the barrier thickness value decreases to 3.75 nm.

In order to obtain a reasonable explanation for the abnormally low EQE value of the solar cell with 3.75-nm thick barrier layer, the X-ray diffraction (XRD) is used to examine the crystal quality of InGaN MQW. Figure 3 shows the high resolution (0002) ω–2θ X-ray diffraction (XRD) curves for the samples A, B, and C. The curves clearly show higher-order satellite diffraction peaks of the superlattices, indicating a good layer periodicity of these superlattices. In order to further characterize the quality of InGaN, the rocking curves through (0002) reflections are measured for InGaN layers. The values of full width at half maximum (FWHM) for InGaN layers in samples A, B, and C are close to 300 arcsec (as shown in the inset of Fig. 3, where the FWHM of sample A is slightly larger than the ones of samples B and C, which may be attributed to run-to-run variations in the MOCVD growth) indicating that each of the samples has a good crystal quality of InGaN MQW.

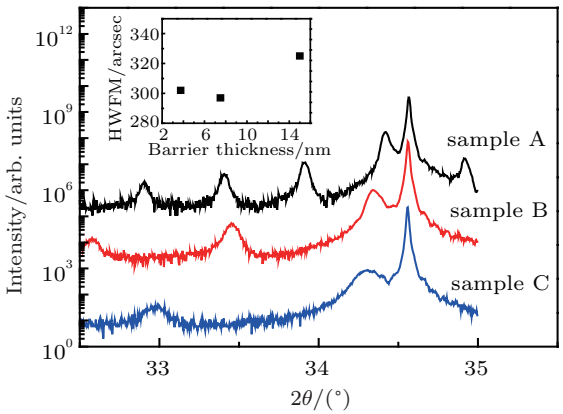


Fig. 3. (color online) The (0002) ω–2θ XRD scan of InGaN/GaN solar cells with different barrier thickness values (The inset shows the full width at half maximum (FWHM) of the InGaN (0002) reflection as a function of barrier thickness).

EL has been widely used as a tool to study the properties of a diode device.[11] The EL peak intensity can be largely affected by the crystal quality of the MQW. In addition, the carrier injection and transport, the quantum confinement ability of carriers, and the polarization effect of MQWs also have

great influences on EL peak intensity. But the PL peak intensity is mainly affected by the characteristics of the MQW. In this work, the EL spectra of InGaN/GaN MQW solar cells are measured at room temperature and with the forward current of 20 mA, and the PL spectra measurements are performed at room temperature using an He–Cd laser with a wavelength of 325 nm as an excitation source. The results are shown in Fig. 4. It is found that the EL peak intensity of sample C is much weaker than those of sample A and sample B, while the PL peak intensity of sample C is relatively strong (as shown in the inset of Fig. 4). It is stronger than that of sample A, but a little weaker than that of sample B. This result indicates that the reduction of EL peak intensity of sample C is not caused by the poor crystal quality of MQWs or the weaker carrier quantum confinement ability. In fact, when the barrier thickness decreases, the piezoelectric polarization of QW will be weaker due to the reduced strain of QW,[12,13] the total electric field in the MQW region (its direction is opposite to the direction of built-in electric field) decreases, and the tilt (slope) of the energy band of the quantum well decreases as shown in Fig. 1, which should result in an increase in the overlap integral of electron and hole wave functions, thus the radiative recombination should be enhanced.[14] So the weak EL peak intensity of sample C should not be caused by the polarization effect of MQW. It is known that the EL peak intensity can partially be influenced by the charge carrier injection and transport in solar cells. If the sample has a poorer quality of p-type GaN layer with a smaller effective p-type doping concentration, the EL peak intensity will be weaker because few holes can be injected into the active region. Combine the results shown in Figs. 2 and 4, then we will be aware that the explanation that the low EQE value of sample C may result from a relatively low efficiency doping concentration of p-type GaN layer is reasonable.

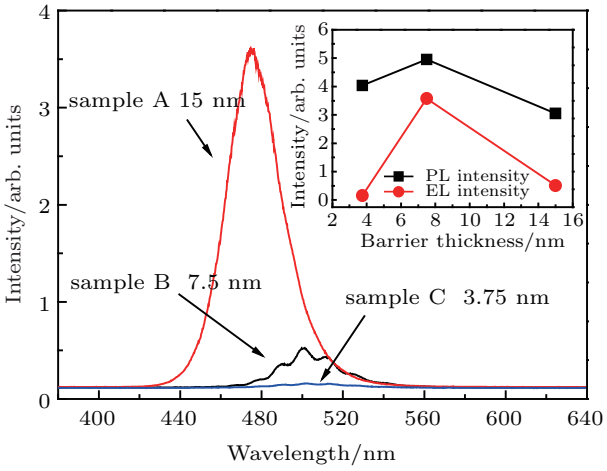


Fig. 4. (color online) EL spectra of InGaN/GaN MQW solar cells (the inset shows the EL and PL peak intensities each as a function of barrier thickness).

In order to check the efficient doping concentration of the p-type GaN layer, the current–voltage (I–V) measurement based on the circular transmission line model (CTLM)[15,16] is used to calculate the resistivity ρ (Ω·cm) of the p-type GaN layer. In this method, the voltage drop is measured by forcing a constant current through the neighboring pads on both sides of the intermediate semiconductor layer, resulting in the so-called CTLM I–V curve. A nominal total resistance value (R_t) can be obtained from the slope of the CTLM I–V curve. In this work, the CTLM patterns are designed with a constant inner radius $r = 200$ μm and the values of circular gap (spacing) d being 15, 20, 25, 30, 35, 40, 50, and 60 μm, respectively. The I–V characteristics of the CTLM patterns are measured using the Keithley 6430. The CTLM patterns are accomplished by the conventional thin film deposition and photolithographic lift-off processes.

Figure 5 shows the CTLM I–V measurements for the samples A, B, and C when the line spacing of the CTLM pattern is fixed at 50 μm. It is noteworthy that all of the CTLM I–V curves exhibit linear characteristics, indicating the ohmic contact between the semitransparent Ni/Au layer and p-GaN. According to the CTLM I–V curves of all circular gaps, the linear relationship between the total resistance value R_t and the $\ln(R/r)$ can be obtained, where R is the outer circular diameter of the CTLM patterns. The values of resistivity ρ (Ω·cm) of p-type GaN layer of samples A, B, and C are calculated from the slopes of these linear relationships respectively. The resistivity value of sample C is about 70 times larger than those of sample A and sample B, i.e., the efficient doping concentration of p-type GaN region of sample C is much lower than those of sample A and sample B.

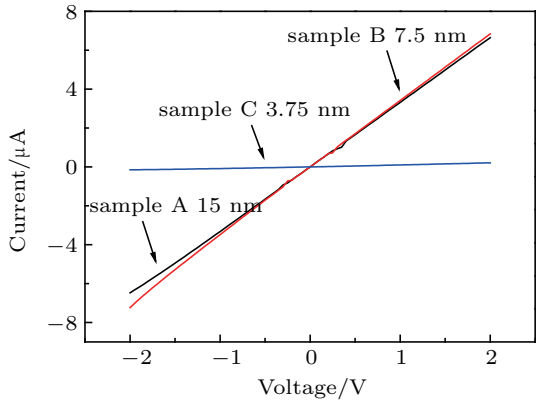


Fig. 5. (color online) CTLM I–V measurements for the samples A, B, and C when the line spacing of the CTLM pattern is fixed as 50 μm.

According to our experimental results, we are aware that a low spectral response of sample C on the lower energy side ($\lambda > 370$ nm) may be due to the low efficient doping concentration of p-type GaN layer, which results in a relatively narrow depletion region of the MQW region. In this case, the photo-generated carriers from a large number of InGaN

QWs may not be able to collected by electrodes due to lacking the positive direction electric field, which may lead to a relatively low EQE value of sample C on the lower energy side ($\lambda > 370$ nm), under the zero valued applied bias. But the depletion region of a p–n junction will widen on both sides of the interface when the reverse-bias increases, and it tends to become wider and extend into the region with lower doping concentration of the junction.

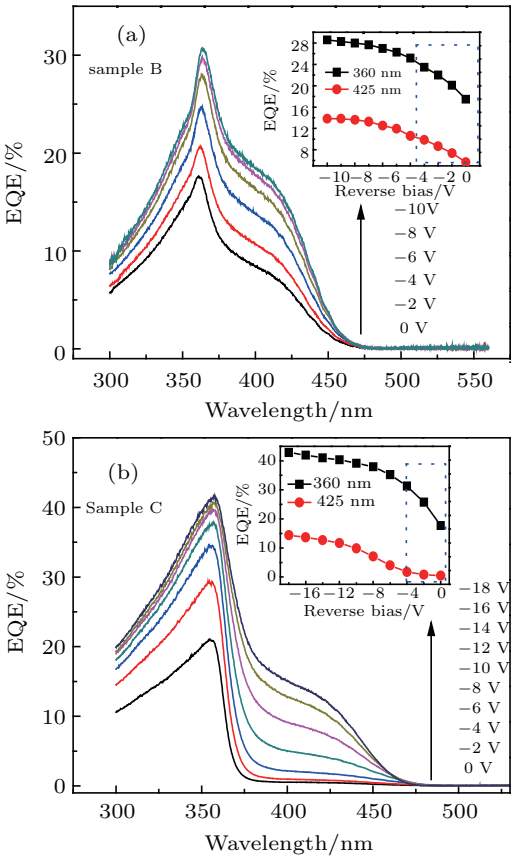


Fig. 6. (color online) Variations of EQE (λ) value of the InGaN/GaN MQW solar cells with wavelength at different reverse-bias voltages for samples B (a) and C (b). The insets show the dependences of EQE value on reverse-bias voltage for samples B and C at wavelengths of 360 nm and 425 nm.

In order to further verify the viewpoint that the low EQE value of sample C is due to the low efficient doping concentration of p-type GaN layer, the EQE spectra of samples B and C under several biased conditions are measured, and the results are shown in Fig. 6. From Fig. 6(a) it follows that for sample B the EQEs of all wavelengths increase with reverse-bias increasing, and they become saturated when the reverse-bias increases to -10 V. But the dependences of EQE on the reverse-bias for sample C are different as shown in Fig. 6(b). When the reverse-bias increases from zero to -4 V, the EQE increases rapidly on the high energy ($\lambda < 370$ nm) side, but only slightly increases on the low energy ($\lambda > 370$ nm) side. Then the EQE increases quickly on the low energy side, but increases slowly on the high energy side when the reverse-bias increases from -6 V to -14 V. Finally, the EQEs of all wavelengths are nearly saturated when the reverse-bias increases to -16 V. Such behaviors of EQE exhibit different extension features of the depletion regions on both sides of the junction interface under non-zero valued applied reverse-bias voltages. The insets of Fig. 6 show the dependences of EQE on reserve bias at two different wavelengths of 360 nm (square points) and 425 nm (circular points). The insets clearly show the difference in reverse-bias dependence of EQE between sample B and sample C, especially when the reverse-bias increases from 0 V to -4 V. For sample B, the values of EQE at 360 nm and 425 nm are increased by 7% and 5% respectively, while they are increased by 14% and 1% for sample C, respectively.

The results of Fig. 6 indicate that for sample B, the EQE enhancement of all wavelengths is due to the depletion region extending into both the MQWs region and p-type region simultaneously with the increase of reverse-bias. But for sample C, due to a relatively low efficient p-doping concentration of p-type GaN, the depletion region extends rapidly first into the p-type region, and then it extends into MQWs region when the p-type region is almost totally depleted. These results can well support the viewpoint that a weak spectral response at the zero bias of sample C is due to the low efficient doping concentration of the p-type GaN layer.

4. Summary

The external quantum efficiencies of InGaN/GaN MQW solar cells with three different values of barrier thickness (15 nm, 7.5 nm, 3.75 nm) are investigated in detail. It is found that the solar cell with a 7.5-nm thick barrier exhibits the best photovoltaic properties, which may be caused by the reduction of the piezoelectric polarization of MQW and the enhancement of tunneling effect of photo-generated carriers in MQWs when the barrier thickness value decreases from 15 nm to 7.5 nm. But due to the low efficient doping concentration of p-type GaN, the depletion width of the MQW region decreases, which causes the carriers generated from a large number of InGaN QWs to fail to be collected by the electrodes and the EQE of the solar cell with the 3.75-nm thick barrier layer decreases to nearly zero on the low energy side ($\lambda > 370$ nm).

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