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Pulsed laser deposition of Nd:YAG on Si with substrate bias voltage

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Abstract

Polycrystalline yttrium aluminum garnet ($Y_3Al_5O_{12}$) thin films doped with neodymium have been prepared by the pulsed laser deposition (PLD) method on (1 1 1)-oriented Si wafers. Effect of external DC electrical field applied between substrate and target on the crystal quality was investigated. The growth process was carried out at a rather moderate substrate temperature of 500 °C. Obtained films were characterized by the X-ray diffraction (XRD) complete with radioluminescence spectroscopy (RLS). Intensive radioluminescence spectra of such films are reported for the first time. Laser-produced plasma plume investigations by means of time-of-flight (TOF) mass spectrometer were performed as well. Obtained results clearly indicate that the chemical composition of the plasma plume depends on the target–substrate bias voltage.

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Keywords: Plasma processing; Epitaxy; Growth

1. Introduction

Studies of neodymium-doped thin films of YAG focus much interest due to their technological applications in optoelectronic systems. Growth of the doped material is found to be much more difficult than the undoped one because of the fact that doping with Nd^{3+} ions decreases stability of the fourfold coordination of aluminum within the YAG lattice. Polycrystalline Nd-doped $Y_3Al_5O_{12}$ ceramics show highly efficient laser oscillations at 1064 nm bringing an alternative to Nd:YAG single crystals [1]. Several deposition techniques were employed to deposit Nd:YAG thin films, but only a few publications on pulsed laser deposition (PLD) of YAG have been reported [2,3]. Another optical thin garnet films were also successfully fabricated by PLD [4–8]. Presented paper deals with experimental investigation of the post-plasma plume and the quality of the deposited layer, which were influenced by external electric field. The technique of the plume characterization is based on the time-of-flight (TOF) spectroscopy. In order to understand physical processes in such a plume, TOF spectra are measured at different experimental conditions. Then, they are analyzed in terms of the chemical

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composition of the plume depending on the target–substrate distance and on the bias voltage. Influence of the latter parameter on a deposition temperature and a film growth rate is reported in other papers [4], but changes in post-plasma plume under the external electric voltage are still unexplained.

Apart from X-ray diffraction (XRD) and TOF measurements, quality of the films is assessed additionally by means of radioluminescence spectroscopy (RLS). The emission lines due to the $4f^3$ intra-configuration transitions of Nd^{3+} ions are identified and analyzed. The structural dependence of Nd:YAG layer on the substrate temperature and on the substrate–target electric field is also taken under consideration.

2. Experimental

The neodymium-doped YAG films have been deposited using the standard experimental set-up described elsewhere [9]. The process was carried out in a stainless-steel vacuum chamber under the pressure of 10^{-6} mbar. Vaporized target contained high-purity powders of Y_2O_3, Al_2O_3 and 1% of Nd_2O_3 supplied by Aldrich Chemical. Ablation was made possible thanks to a XeCl excimer laser beam of the following parameters: $\lambda = 308$ nm, $\tau = 20$ ns, repetition rate = 10 Hz, fluency = 5 J/cm^2, and the gaseous species were deposited on (1 1 1)-oriented Si substrates. Substrate holder was placed 4 cm over the target being parallel to its surface. The target rotational speed was about 18 rounds per minute. The area of Nd:YAG films was typically 1.5 cm^2 and their thickness was 200–400 nm. The lattice mismatch which is defined by $(a_{\mathrm{Nd:YAG}} - 2a_{\mathrm{Si}})/2a_{\mathrm{Si}}$ is about 11%, where $a_{\mathrm{Nd:YAG}}$ and a_{Si} are lattice constants of Nd:YAG and Si, respectively [10].

Structural features of the films were analyzed according to their room-temperature XRD and radioluminescence spectra. Diffraction experiments were carried out using Siemens D5000 powder diffractometer (Kα (Cu) = 1.54 nm), while the latter were recorded in the system composed of an X-ray tube operated continuously at 35 kV and 25 mA, a monochromator (Acton Research SpectraPro-500), Hamamatsu R928 photomultiplier and a PC computer with an A–D card to control the experiment and store the data [11].

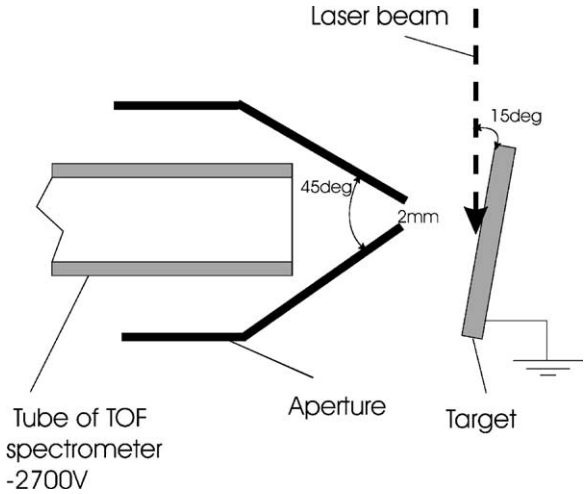

Fig. 1. Schematic geometry for the laser ablation and ion detection experiments.

To investigate the plasma plume that arise from the target material, ion TOF mass spectrometer (COMSTOCK, model TOF-101) with the intake aperture was used. The resolution of the spectrometer (6.25 ns) was high enough to resolve the spectra of ablated Nd_2O_3, Y_2O_3 and Al_2O_3 that were detected shot-to-shot by the tandem multichannel plate detector. The signal composed of a train of pulses was amplified and passed to the input of a real-time multichannel scaler (RTMS) [12]. The influence of the bias voltage of the intake aperture on TOF spectra was studied assuming that it exerted an effect similar to that of the substrate one. In the experiment, the distance between the target and the intake aperture of the spectrometer was fixed at 1.5 and 2.5 cm (Fig. 1).

3. Results and discussion

As mentioned previously, attention was drawn to explanation, how TOF spectra of ablated species were affected by the substrate bias voltage. All recorded mass spectra were cumulatively collected during 500 laser shots. Although many various ions were observed in TOF spectra of oxides in post, only those of yttrium oxide contained lines characteristic of N^+ and $C_2{}^+$ ions. This can be explained by strong contamination of Y_2O_3 with both CO_2 and NH_3 molecules from air. The spectra were measured for the two

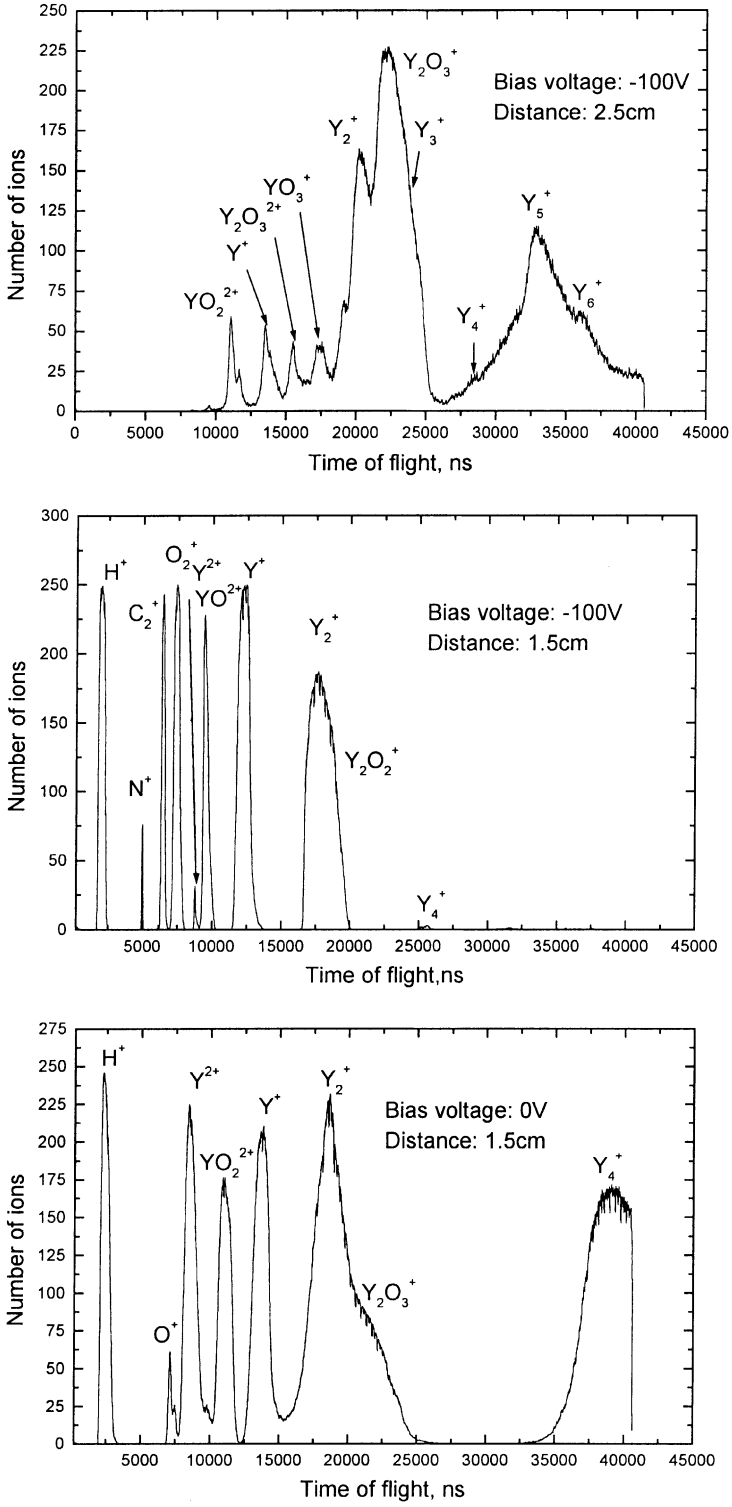

Fig. 2. TOF mass spectra generated from laser ablation of cold pressed Y_2O_3 powder for different bias voltage on intake aperture of spectrometer and distance between target and aperture.

different positions of spectrometer intake aperture over the target. In Fig. 2 the mass distribution of positive ions in the plasma plume sputtered from Y_2O_3 target is shown. For the lower distance, the plume contained small quantities of oxides, while for the bigger one strong reduction in Y^+ signal intensity is observed. This is due to the atom → cluster conversion process [13]. In addition, when the bias voltage used for the acceleration of positive ions was increased, the mass spectrum of Y_2O_3 powder revealed decrease in the mass signal of heavy ions. On the other hand, similar results were achieved if the intake aperture was placed closer to the target, even if the bias voltage was kept constant. Observed facts could be explained in terms of bias-induced ordering of the ion beam.

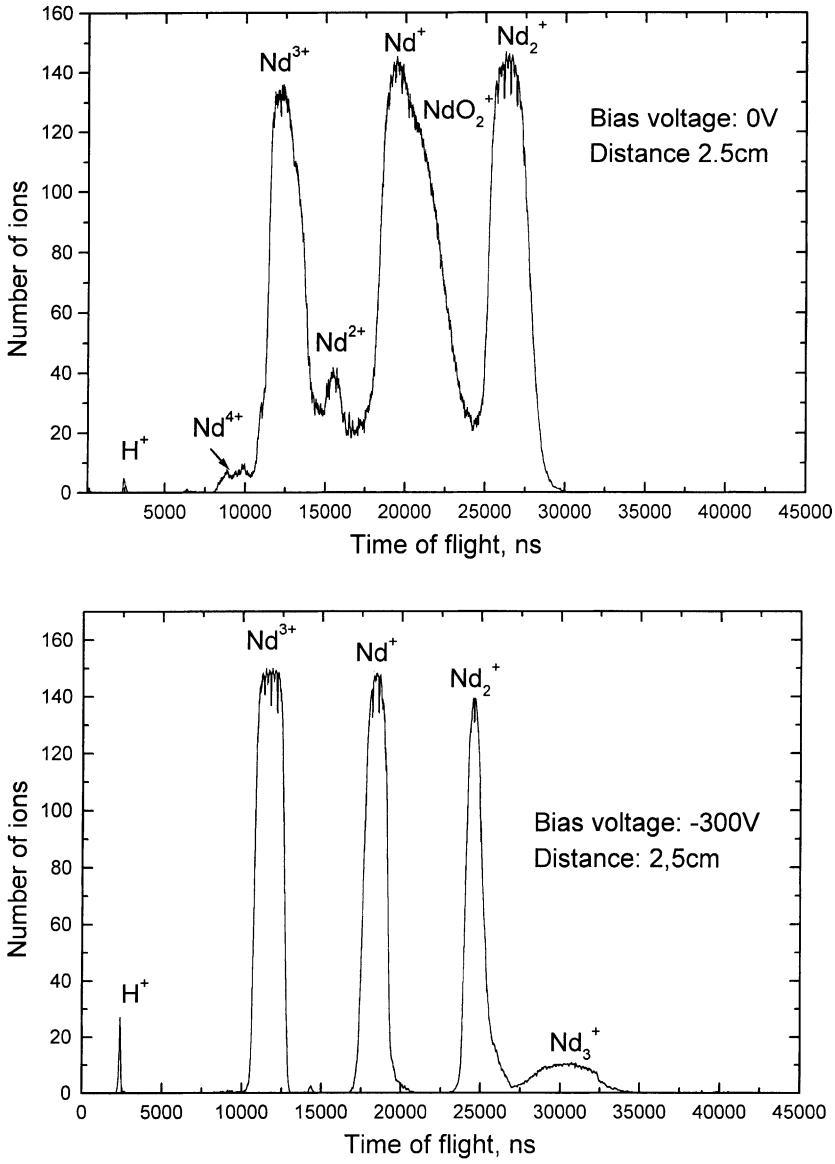

Fig. 3. TOF mass spectra of Nd_2O_3 powder for two bias voltage on the intake aperture. The distance between the target and the aperture of the spectrometer was 2.5 cm.

Ions sputtered from the target form molecular beam, part of which is passed through the target–substrate distance and reached the mass detector. Under non-biased conditions the ions move in all possible directions and collide to each other. In such a case, they can easily stick that converts small radicals into heavy clusters. Indeed, many various lines of considerable widths, including those of heavy ions, are characteristic of the TOF spectra measured without any DC polarization. In contrast, strong electric field forces the

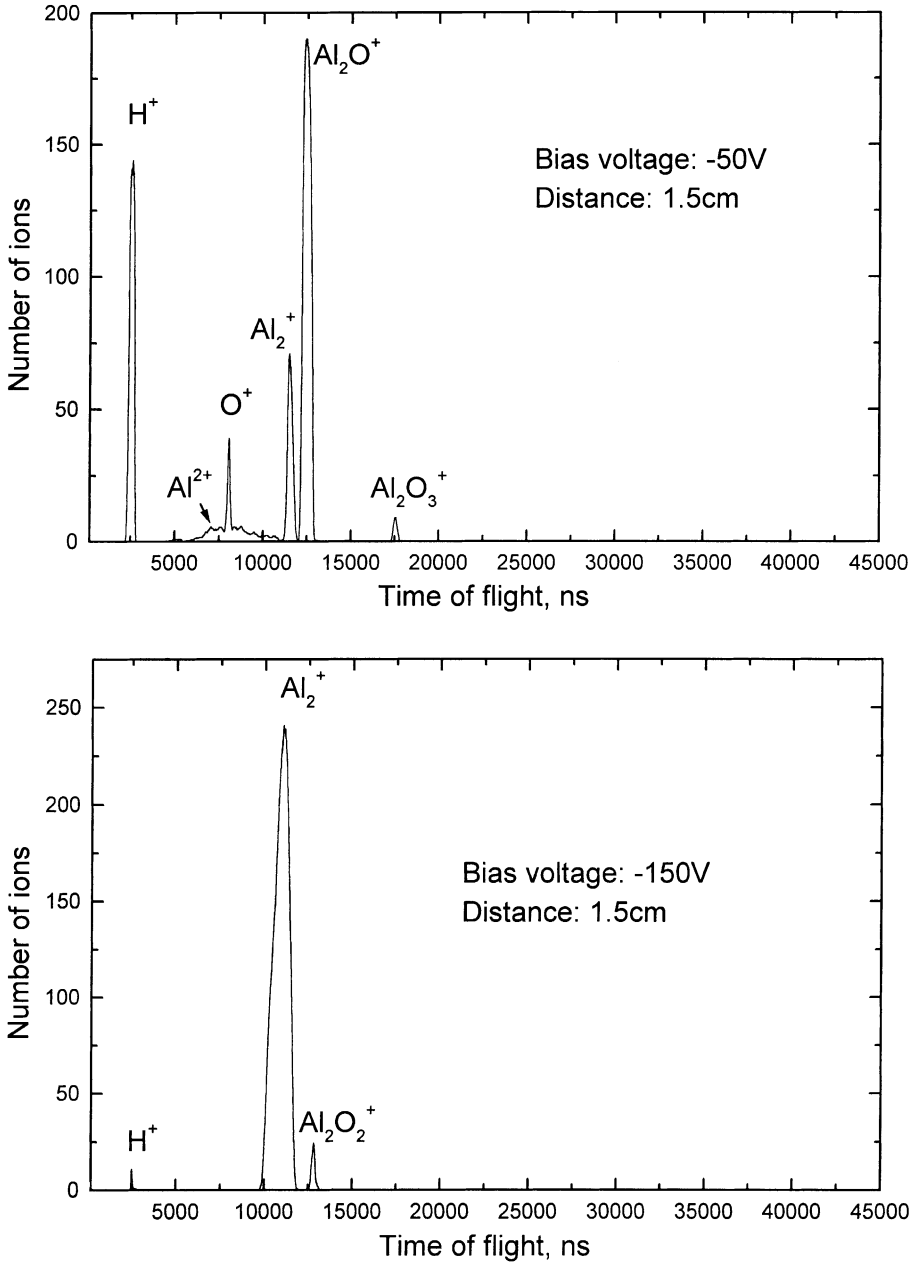

Fig. 4. TOF mass spectra of Al_2O_3 for two bias-voltage values applied to the intake aperture. The distance between target and the aperture of the spectrometer was 1.5 cm.

proper orientation of the beam that makes the ions to move in an ordered way. This implies that ions collide infrequently and therefore atom to cluster conversion rate is suppressed. As a result, number of lines in appropriate TOF spectra is reduced, with the lines being generally narrower compared to those observed under non-biased conditions.

In Figs. 3 and 4 TOF spectra of Nd_2O_3 and Al_2O_3 for different bias voltages are presented. Improved quality of plasma, following from the smaller number of clusters, was found to appear with increasing bias voltage, and therefore the films obtained with the substrate bias exhibited better radioluminescence properties. In the previous paper [14] that was devoted to influence of heat treatment on the quality of Nd:YAG films, detailed analysis of XRD spectra have been presented. In Fig. 5 diffraction patterns taken from both the biased and unbiased Nd:YAG thin films are shown. It appears that only the one deposited under polarization conditions exhibits $Y_3Al_5O_{12}$ diffraction peaks. There are the following XRD peaks characteristic of YAG structure: 29.26°, which corresponds to (4 0 0) crystal planes and 33.83°, which corresponds to the (4 2 0) reflection. Bias-induced crystallization of the YAG phase is caused by increase in the plasma plume energy that is sufficiently high to make possible surface diffusion the particles. Therefore, under bias conditions incident ions may subsequently diffuse over the surface to find local potential energy minima. In turn, particles that reach the growth region under non-biased conditions rapidly stick to the given surface sites since they are mostly low-energy heavy clusters. On account of that, films deposited without bias are in general amorphous, but those of electrically polarized exhibit rather polycrystalline structure. Obtained results are in agreement with previous observations that have been made during experiments on thin metallic films deposition.

In Fig. 6 radioluminescence spectra of Nd:YAG thin films for different target–substrate bias voltages are presented. The spectra of the films obtained under the voltage of 500 and 100 V clearly shows sharp lines that are due to $4f^3$ intra-configurational transitions of the Nd^{3+} ion. The lines, at about 430, 480 and 550 nm, correspond to transitions that originate from lower levels. There is, as expected, no d–f emission but there are also some missing f–f emission lines that originate from some higher levels of the $4f^3$ configuration and are usually visible in the Nd:YAG monocrystal radioluminescence spectra. The spectrum shows also some broad band emission at 300 to 400 nm that could represent the so-called ‘‘host’’ emission, characteristic

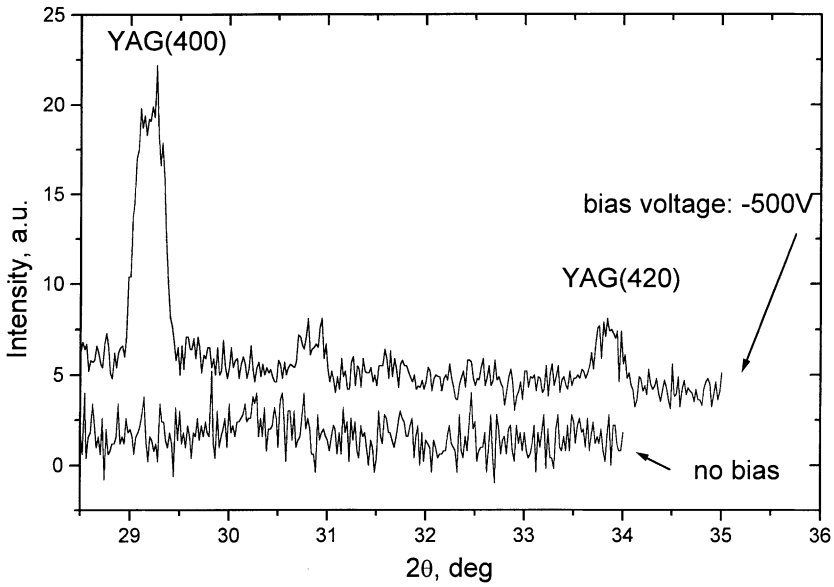

Fig. 5. The dependence of XRD patterns of Nd:YAG thin films on the substrate bias voltage. The substrate temperature was 500 °C.

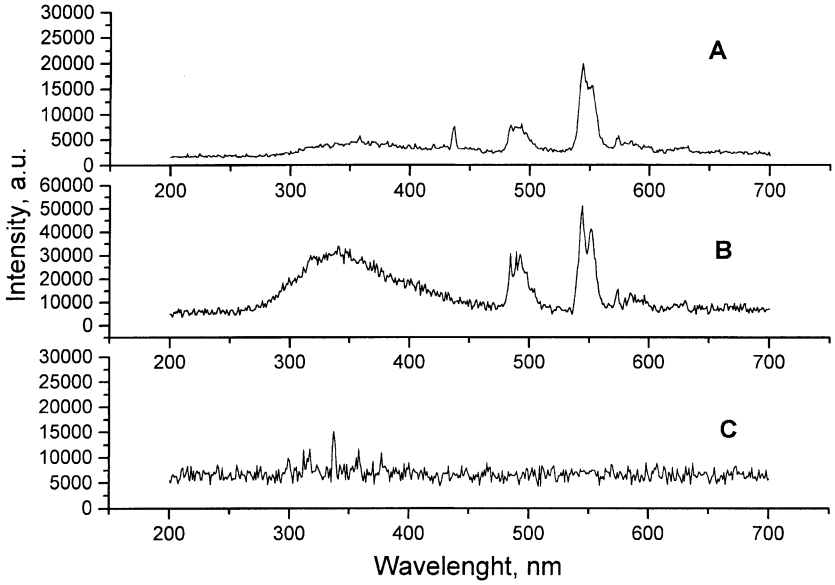

Fig. 6. Radioluminescence spectra of Nd:YAG thin films. The substrate temperature of all samples was 500 °C. The substrate bias-voltages are as follows: (A) −500 V; (B) −100 V; (C) no substrate bias.

of the undoped YAG. Interestingly, the spectrum of the Nd:YAG film obtained without the substrate bias shows no emission at all.

4. Conclusion

In the presented work, the Nd:YAG thin films on (1 1 1)-oriented Si substrates have been deposited by the PLD method with the electrical field applied between the target and the substrate. These films were proved to possess some interesting structural and electronic properties that were determined using an X-ray diffractometry supported by the RLS. The absence of some f–f emission lines in radioluminescence of Nd:YAG films that are present in the spectrum of Nd:YAG monocrystals calls for further studies. This observation could potentially provide new and interesting information about quenching/energy transfer processes that are of importance in the considered field. It is also interesting to note that radioluminescence can potentially provide a convenient measure of the film quality. The analysis of the TOF spectra provides evidence of the positive influence of the substrate bias voltage on the quality of films.

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