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SPECIAL TOPICS

Temperature dependent self-compensation in Al- and Ga-doped $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ thin films grown by pulsed laser deposition

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We studied the doping efficiency of Al and Ga dopants in $(\text{Mg,Zn})\text{O}$ alloys as a function of the growth temperature and post growth annealing times. High-temperature growth results in the highest structural quality and highest electron mobility; the doping efficiency is limited by the dopant's solubility. It was investigated in detail that a low growth temperature is needed to achieve free carrier densities above the solubility limit of the dopants. Samples grown at temperatures of 300 °C and below have a free carrier density significantly above the solubility limit yielding the minimum resistivity of $\rho_{\min} = 4.8 \times 10^{-4} \Omega \text{ cm}$ for $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Al}$ thin films grown on glass at 300 °C. Annealing of these samples reduces the free carrier density and the absorption edge to values similar to those of samples grown at high temperatures. The saturation of the free carrier density and the optical bandgap at their high temperature growth/annealing values is explained by the thermal creation of acceptor-like compensating defects in thermodynamic equilibrium. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4968544>]

I. INTRODUCTION

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is a suitable material for transparent electrode applications for, e.g., thin film solar cells^{1,2} due to its large and tunable bandgap, easy *n*-type dopability, and natural abundance.³ Recently, new world-record efficiency of 15.5% for pure-sulfide $\text{Cu}(\text{In,Ga})\text{S}_2$ thin film solar cell has been reported, where $(\text{Mg,Zn})\text{O}$ was used as a buffer layer.⁴ The bandgap of wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ can be systematically tuned from 3.3 eV up to 4.2 eV by changing the composition in the range of $0 < x < 0.44$ ³ allowing the band alignment to be optimized at the interface between the transparent electrode and buffer or the active layers.⁵ Detrimentally, an increased Mg content in the $(\text{Mg,Zn})\text{O}$ alloy reduces the conductivity, which can to some extent be modified by extrinsic doping, e.g., introducing group-III elements such as Al or Ga.^{6,7} However, there are requisites for the doping of semiconductors, summarised by Zhang *et al.*: (i) shallowness of the dopant energy levels in the sense of small thermal activation energy such that these dopants are ionised at room temperature (RT); (ii) solubility limit of impurities in the host material, which affects the formation of secondary crystallographic phases; and (iii) formation of intrinsic compensating defects.⁸ In our recent studies⁹ on Al and Ga-doped wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys, we showed that thin films grown at an elevated temperature of 600 °C with a dopant concentration of up to $N_d \approx 2.5 \text{ at.}\% \hat{=} 1 \times 10^{21} \text{ cm}^{-3}$ revealed a high doping efficiency. Beyond that value, the structural and the electrical properties sharply deteriorate, and the doping efficiency drops. Hence, the free carrier concentration cannot be increased by adding additional donors. Here, the influence of the growth and annealing temperatures on the doping efficiency of Al- and Ga-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films was

studied to circumvent this limitation. For this purpose, samples were deposited at different growth temperatures and post-annealed in a vacuum at 400 °C.

II. EXPERIMENTAL DETAILS

$\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{Al}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{Ga}$ thin films were grown on glass and *c*-plane or *r*-plane sapphire substrates by pulsed laser deposition (PLD) using a continuous composition spread method (CCS)^{9,10} to vary the alloy composition and dopant concentration continuously. The films were deposited at different growth temperatures of $T_g = 25^\circ\text{C}$, 200 °C, 300 °C, and 600 °C; otherwise, the same growth conditions as in another important study⁹ were used. The chemical composition was investigated by energy dispersive X-ray spectroscopy (EDX, FEI NovaLab 200). In order to increase the accuracy of the EDX data, e.g., by reducing the influence of the X-ray signal from the substrate, reduced acceleration voltages were used. From the large material library created by the CCS method, thin films with fixed chemical composition that corresponds to an optimal⁹ Al/Ga dopant concentration of 2.5 at.% and with a Mg alloy content of $x = 0.05$, were chosen. Note that all our investigated samples have a similar size of about $(5 \times 5) \text{ mm}^2$, where the variation of the chemical composition within such a piece is about $\pm 0.4 \text{ at.}\%$ at most for the Mg-content and the dopant concentration. The thickness of the films was determined using spectroscopic ellipsometry to be between 150 and 350 nm. Note that this large thickness variation is due to the variation of the growth rate at different T_g . In general, higher growth rates are observed for lower T_g . For a given T_g , the thickness variation is about $\pm 20\%$ at most for all CCS thin films investigated.

The electrical properties were investigated by Hall effect measurement at room temperature (RT) using the van der Pauw method. Gold, sputtered through a shadow mask on

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the corners of the samples, was used as an ohmic contact. The absorption edge of the films is obtained by applying a Tauc plot to transmission data and by line shape modeling of spectroscopic ellipsometry data (for further details, see the [supplementary material](#)). Furthermore, the effective electron masses, the crystalline quality, and surface morphology of selected samples were determined by the infrared spectroscopic ellipsometry (IRVASE; see [supplementary material](#) for further details), X-ray diffraction (XRD), and atomic force microscopy (AFM; see [supplementary material](#)) techniques, respectively.

III. RESULTS AND DISCUSSION

From XRD data, no hints as to the appearance of MgO, Al₂O₃, or Ga₂O₃ phases in all thin films investigated were found, as shown in Figure 1 for Al- and Ga-doped Mg_{0.05}Zn_{0.95}O thin films grown at 200 °C and post-annealed in a vacuum at 400 °C. This suggests a good incorporation of Mg as well as Al or Ga ions into the cation (zinc) sites of ZnO.

FIG. 1. Wide-angle XRD $2\theta - \omega$ scans for (a) Al- and (b) Ga-doped Mg_{0.05}Zn_{0.95}O thin films with a thickness of 270 nm and 360 nm, respectively. These samples were grown at 200 °C, and post-annealed in a vacuum at 400 °C. Note that the measurements data for annealed films were taken after the final annealing step (~ 6 h). The Au contacts used for the Hall-effect measurement cause the (111)-Au reflexion.

Note that the estimated grain size D along the growth direction, i.e., determined using FWHM values of (002) reflection peaks and the Debye–Scherrer formula,⁹ are similar, being $D \approx 35 \pm 5$ nm for both samples, showing no changes post-annealing. All films showed only the (002) reflection of ZnO, and the peak position of the (002) reflection slightly shifted to higher angles as a result of post-annealing. Chang *et al.* also observed this behavior when Al-doped ZnO thin films grown at $T_g = 200$ °C were post-annealed at 500 °C.¹¹ They argued that the residual stress of the films could be reduced by annealing, which resulted in a peak-shift toward higher angles.

The electrical transport properties of both Al- and Ga-doped (Mg,Zn)O thin films show a strong dependency on T_g . In the Al-doping series, the free charge carrier density (n) and the doping efficiency ($N_{d,act}$) initially slightly increase with growth temperature up to $T_g = 200$ °C, where n reached a maximum value of $8.2 \times 10^{20} \text{ cm}^{-3}$ with a doping efficiency of $N_{d,act} \approx 0.8$, a Hall mobility of $\mu_{Hall} = 13.3 \text{ cm}^2/\text{Vs}$, and a resistivity of $\rho = 5.7 \times 10^{-4} \Omega \text{ cm}$. Further increases of the growth temperature lead to a decrease of n as well as $N_{d,act}$ (cf. Figure 2(a)). Unlike in the Ga-doping series, the films grown at the highest temperatures show highest n and $N_{d,act}$ values. Despite the equality of the dopant concentration, the free carrier densities of Ga-doped samples grown at $T_g \leq 300$ °C are substantially lower than the values determined for Al-doped

FIG. 2. Free charge carrier density, mobility, and estimated doping efficiency, i.e., $N_{d,act} = n/[Al]$ (or $n/[Ga]$), as a function of growth temperature for (a) Al- and (b) Ga-doped Mg_{0.05}Zn_{0.95}O thin films. The dashed lines are a guide for the eye.

samples grown at the same temperatures. Although for the Al-series, the free charge carrier density is almost independent of growth temperature for $T_g \leq 300^\circ\text{C}$, it systematically increases for the Ga-series with increasing T_g . It has been shown that for growth temperatures below 300°C , the doping efficiency of Ga is reduced due to the formation of the Ga_2O_3 phase.¹² In our samples, we did not observe a secondary Ga_2O_3 phase, indicating that the crystallites are too small to be detected by XRD, or that other reasons for the thermal activation of the Ga dopants have to be considered. In the Al-doping series, the maximum n and $N_{\text{d,act}}$ were obtained at $T_g = 200^\circ\text{C}$, where such a maximum may also occur for Ga-doping at around $T_g = 450^\circ\text{C}$ (cf. Figure 2(b)). For $T_g = 600^\circ\text{C}$, both doping series show very similar $N_{\text{d,act}}$ of about 0.1 with $n = 1.3 \times 10^{20} \text{ cm}^{-3}$ and $n = 8.3 \times 10^{19} \text{ cm}^{-3}$ for the Al- and Ga-doped films, respectively. The carrier mobility (μ_{Hall}) of both doping series depicted a monotonic increase with increasing T_g , reflecting the higher crystallinity of the films grown at higher temperatures.¹³

Figure 3 shows the free charge carrier density of $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Al}/\text{Ga}$ thin films as a function of the annealing time for an annealing temperature of 400°C . n changes as the annealing time increases, where the changes are greater for samples grown at lower temperatures. Moreover, the main

changes occurred within the first hour of the annealing time. In the Al-doping series, e.g., for $T_g \leq 300^\circ\text{C}$, the free charge carrier density starts to decrease, then saturates with increasing annealing time. The saturation values of n are similar to the free charge carrier density of (i) $n_{\text{Hall}} = 1.3 \times 10^{20} \text{ cm}^{-3}$ of the film initially grown at $T_g = 600^\circ\text{C}$ and (ii) the solubility limit of Al in ZnO, i.e., 0.3 at. % $\hat{=} 1.2 \times 10^{20} \text{ cm}^{-3}$, in equilibrium.¹⁴ In the literature, this saturation is explained within the amphoteric defect model by thermal creation of acceptor-like self-compensating defects.^{9,15–17} In the Ga-doping series, e.g., for $T_g < 300^\circ\text{C}$, the free charge carrier density increases and reaches values of $n \approx 1 - 2 \times 10^{20} \text{ cm}^{-3}$ during the first hour of annealing time. This supports our prediction that progressively more Ga ions become electrically active during the heat treatment. Furthermore, n stays constant or shows a slight decrease with increasing annealing time. Hence, similar to the Al-doped films, the saturation values of n are also about $1 \times 10^{20} \text{ cm}^{-3}$. More interestingly, in both doping series, the samples grown at $T_g = 600^\circ\text{C}$ had relatively low free charge carrier densities compared to the dopant concentration, i.e., $N_{\text{d,act}} \approx 0.1$, which remains almost unchanged during the heat treatment (cf. Figure 3). This is probably due to the formation of compensating defects during the growth at high temperatures, which do

FIG. 3. Dependence of the free charge carrier density on the annealing time for (a) Al- and (b) Ga-doped $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ thin films. Post-annealing was performed in a vacuum at 400°C . The lines are a guide for the eye.

FIG. 4. Dependence of the Hall mobility on the annealing time for (a) Al- and (b) Ga-doped $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ thin films. Post-annealing was performed in a vacuum at 400°C . The lines are a guide for the eye.

not change during the post-annealing. As shown in Figure 4, the mobility also varies as a function of the annealing time. In the Al-doping series, the Hall mobility decreases as a result of post-annealing. Apparently, the formed intrinsic defects compensate for the free charge carriers and reduce the mobility through ionised impurity scattering. In the Ga-doping series, the Hall mobility of the RT grown sample first slightly decreases, and then saturates with increasing annealing time. The initial decrease in mobility could be underestimated due to the higher uncertainty of the experimental data caused by the high resistivity of the as-grown sample, which lies at the boundary of the Hall-effect measurements. In the samples grown at 200 °C and 300 °C, the mobility increases within the first 60 min of the post-annealing process, and then saturates or slightly decreases. This can be explained as follows. First, increasingly more Ga ions become electrically active and thus contribute free electrons. Consequently, potential barriers at the grain boundaries are screened more effectively; thus, mobility increases.¹³ As is commonly understood, grain boundary scattering should be considered for lower values of n , e.g., $n < 10^{20} \text{ cm}^{-3}$; above this range, the mobility is mainly affected by ionised impurity scattering.^{18,19} Hence, as also found for the Al-doping series, ionised impurity scattering prevents a further increase in mobility as soon as n reaches the value of 10^{20} cm^{-3} . Presumably, ionised impurity scattering is increasingly pronounced in post-annealed films compared to as-grown ones, due to the increased density of the acceptor-like native defects, which are formed at high growth temperatures or during the post-annealing.

In Figure 5, the free carrier density, the doping efficiency, and the absorption edge are plotted as a function of the growth and/or annealing temperature. Note that the symbols that represent the annealed samples are labelled with the letter “A.” For comparison to our data, literature values on $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ for $0 \leq x(\text{Mg}) \leq 0.1$ are also included. Despite the different growth methods and conditions used, a distinct dependence is obvious. It turns out that the free carrier density is about 10 times higher for the films grown or annealed at lower temperatures (i.e., up to 400 °C) compared to those of high-temperature grown/annealed ones. The highest doping efficiency was also observed for lower growth temperature; it tends to decrease with increasing growth/annealing temperature. Zakutayev *et al.* also found that the samples grown at lower growth temperatures exhibit higher conductivity than high-temperature (>500 °C) grown ones.⁴⁰ It has been argued that the former samples are in a non-equilibrium state, whereas the latter are in thermodynamic equilibrium. Correspondingly and in good agreement with the electrical data, the absorption edge also shows the strongest Burstein–Moss shift (BM-shift) for the films grown at $T_g \leq 400$ °C (cf. Figure 5(c)). Note that the share of the Mg incorporation to the bandgap shift in the alloy, $\Delta E_g^{\text{Mg}}(x)$, is subtracted using Eqs. (2) and (3), in order to see the influence of the growth/annealing temperature on the BM-shift. The samples grown above 400 °C showed a similar absorption edge of about 3.5 ± 0.1 eV, which is consistent with the absorption edge values that were obtained for annealed films (Table I).

FIG. 5. (a) Free carrier density, and (b) estimated doping efficiency versus growth/annealing temperature. Al- and Ga-doped films are given with green and blue symbols, respectively. Note that the films presented with filled symbols have the dopant concentration of >1 at. % (mostly ≥ 2 at. %), where the films with ≤ 1 at. % are given with open symbols. (c) Absorption edge versus free charge carrier density for different growth/annealing temperatures. The share of the Mg incorporation to the bandgap shift of the alloys was subtracted by using Eqs. (2) and (3). The symbols that indicate the annealed samples are labelled with the letter “A.” The dashed lines and grey area are guides for the eye. Literature data are taken from Refs. 6,7,9, and 20–39. Note that the absorption edge values were mainly obtained from transmission data, except for the data of Ref. 31 and this study, where ellipsometry data were also used.

In order to compare these experimentally determined absorption edge energies, we calculated the intrinsic, non-screened optical bandgap by taking into account a value of the BM-shift for $n = 1.2 \times 10^{20} \text{ cm}^{-3}$ using the following formula:

$$\Delta E_g^{\text{BM}} = \frac{\hbar^2}{2m_r^*} (3\pi^2 n)^{2/3}, \quad (1)$$

TABLE I. Free charge carrier density and the absorption edge of $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:(\text{Al}/\text{Ga})$ thin films that have a fixed dopant concentration of $N_d \approx 2.5 \text{ at.}\% \approx 1 \times 10^{21} \text{ cm}^{-3}$. Post-annealing was performed for 6 h in a vacuum at 400°C . The values of the absorption edge determined from transmission and ellipsometry data are in good agreement within about $\pm 0.05 \text{ eV}$; thus, averages are listed. Note that due to the absence of the transmission data, the absorption edge values for as-grown Al-doped films at 25°C and 300°C were not included.

T_g ($^\circ\text{C}$)	Dopant	$n_{\text{as-grown}}$ (10^{20} cm^{-3})	n_{anneal} (10^{20} cm^{-3})	$E_{g,\text{as-grown}}$ (eV)	$E_{g,\text{anneal}}$ (eV)
25	Al	6.8	0.82	...	3.65
200	Al	8.2	2.7	4.05	3.62
300	Al	6.2	2.24	...	3.64
600	Al	1.3	1.38	3.59	3.60
25	Ga	$\sim 10^{-4}$	0.44	3.41	3.65
200	Ga	0.04	0.61	3.37	3.55
300	Ga	0.92	1.6	3.54	3.64
600	Ga	0.83	0.97	3.61	3.61

and by taking into account

$$\Delta E_g = \Delta E_g^{\text{BM}} + \Delta E_g^{\text{Mg}}(x), \quad (2)$$

and

$$\Delta E_g^{\text{Mg}}(x) = 3.339 + 1.241x + 1.89x^2, \quad (3)$$

where ΔE_g is the change of optical bandgap due to the BM shift, ΔE_g^{BM} , and Mg alloying, $\Delta E_g^{\text{Mg}}(x)$. $\hbar$ is the Planck constant, and m_r^* is the reduced mass, described by $(1/m_r^*) = (1/m_e^*) + (1/m_h^*)$, where m_e^* and m_h^* are the effective electron and hole masses, respectively. For this calculation, the reduced mass is assumed as $m_r^* \approx m_e^*$, being only valid for $m_e^* \ll m_h^*$, and using the effective mass of $m_e^* = 0.3 m_e$ of ZnO and also $m_e^* = 0.4 m_e$ which was experimentally obtained for Al and Ga-doped films grown at $T_g = 600^\circ\text{C}$. As a result, BM shift values are found to be 0.3 eV and 0.22 eV for $m_r^* = 0.3 m_e$ and $m_r^* = 0.4 m_e$ values, respectively. From Eq. (3), the share of the Mg incorporation to the bandgap shift in the alloy, $\Delta E_g^{\text{Mg}}(x)$ is found to be $\approx 0.07 \text{ eV}$ for $x = 0.05$. Hence, the total increase of the optical bandgap, i.e., for $n = 1.2 \times 10^{20} \text{ cm}^{-3}$, is about $0.3 \pm 0.1 \text{ eV}$, which is in good agreement with experimental results (cf. Table I and Figure 5(c)). An explanation for this approaching-constant value of the optical bandgap at $3.5 \pm 0.1 \text{ eV}$ is that under equilibrium conditions, the solubility limit of Al is $0.3 \text{ at.}\%$,¹⁴ corresponding to a maximum free charge carrier density of about $n = 1.2 \times 10^{20} \text{ cm}^{-3}$. This results in a BM shift of about 0.3 eV and hence the optical absorption edge of about $3.3 \text{ eV} + 0.3 \text{ eV} = 3.6 \text{ eV}$. Under equilibrium conditions, we find the maximum density of free carriers in $\text{ZnO}:\text{Al}$ to be $n = 1.2 \times 10^{20} \text{ cm}^{-3}$ and a maximum BM shift of 0.3 eV , corresponding to an optical absorption edge of 3.6 eV . We conclude from these results that the Fermi level pinning energy for the n -type doping case lies about 0.3 eV above the conduction band minimum of ZnO, which is lower than the predicted value of about 1.1 eV .¹⁷

In Figure 6, the free charge carrier density, the mobility, and the resistivity of as-grown $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Al}$ thin films grown on different substrates are plotted as a function of Al

FIG. 6. (a) Free charge carrier density, (b) mobility, and (c) resistivity versus Al concentration for $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Al}$ thin films grown on indicated substrates at different growth temperatures. Blue circles are indications of the minimum resistivity of $\rho_{\min} = 4.8 \times 10^{-4} \Omega \text{ cm}$ with corresponding $n = 6.2 \times 10^{20} \text{ cm}^{-3}$ and $\mu_{\text{Hall}} = 21.2 \text{ cm}^2/\text{Vs}$, which were depicted for the sample grown at $T_g = 300^\circ\text{C}$.

concentration for indicated growth temperatures. It was found that the choice of the substrate is not essential for low-temperature grown thin films. As shown, the samples grown at lower growth temperatures, e.g., $T_g \approx 200^\circ\text{C}$, have very high free charge carrier densities that are close to the 100% ionisation line of the dopant. Presumably, the thermal creation of compensating defects is very low in these films due to the low growth temperatures. On the other hand, samples grown at higher temperatures, e.g., $T_g \approx 600^\circ\text{C}$, have the highest

mobility values. As discussed above, this is mainly related to the improved crystallinity of the films at higher growth temperatures. However, most applications, e.g., thin film solar cells, require transparent electrodes with the lowest possible resistivity, which is obtained by both high free carrier density and high mobility. As shown, the minimum resistivity of $\rho_{\min} = 4.8 \times 10^{-4} \Omega \text{ cm}$, with corresponding $n = 6.2 \times 10^{20} \text{ cm}^{-3}$ and $\mu_{\text{Hall}} = 21.2 \text{ cm}^2/\text{Vs}$, was obtained for the film grown at $T_g = 300^\circ\text{C}$ (Figure 6(c)). Furthermore, the Al concentration in this film is about $1 \times 10^{21} \text{ cm}^{-3} \hat{=} 2.5 \text{ at. \%}$, which is consistent with our previous study showing this range as an optimal doping concentration to prepare transparent electrodes with good transport properties.⁹

IV. CONCLUSIONS

The influence of the growth and annealing temperatures on the doping efficiency of Al- and Ga-doped $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ PLD thin films has been studied and compared to reported literature data. It was found that the films deposited at lower growth temperatures, i.e., $T_g < 400^\circ\text{C}$, have higher free charge carrier density, doping efficiency, and optical bandgap than those initially grown at high temperatures, i.e., $T_g \geq 400^\circ\text{C}$. In addition, when low-temperature, i.e., $T_g \leq 300^\circ\text{C}$, grown films were annealed in a vacuum at 400°C , the free carrier density, as well as the optical bandgap decreased. The films initially grown at high temperature, i.e., $T_g \geq 400^\circ\text{C}$ showed similar (lower) conductivity compared to these annealed films, which can be explained by the thermal creation of acceptor-like compensating defects, most likely V_{Zn} and its complexes.⁴¹ Thus, it is preferable to grow ZnO and (Mg,Zn)O thin films at growth and annealing temperatures below 400°C in order to achieve optimal electrical and optical properties for transparent electrode applications. The minimum resistivity of $\rho_{\min} = 4.8 \times 10^{-4} \Omega \text{ cm}$ was obtained for $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Al}$ thin films grown on glass at 300°C .

SUPPLEMENTARY MATERIAL

In the [supplementary material](#), exemplary spectroscopic ellipsometry and transmission data are shown for $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}:\text{Ga}$ thin film grown at 200°C and post-annealed (about 6 h) in a vacuum at 400°C . In addition, a numerical B-spline model and a parametric model for the dielectric function are given, which were used to obtain the absorption edge values by extrapolating $(E \times \alpha)^2$ against E , where E and α are the photon energy and the absorption coefficient, respectively. Furthermore, the surface morphology and the wide-angle XRD ($2\Theta - \omega$) scans of selected samples are shown for comparison.

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