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Electrical characteristics and pulse degradation of ZnO varistors with Nb_2O_5 dopant

HUI-FENG LI, YU-CHUN XU, SHI-LIANG WANG, LI-QIONG WANG
Solid State Electronics Department, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China

The influence of Nb_2O_5 doping and pre-sintering of Nb_2O_5 with ZnO on electrical and pulse degradation characteristics of ZnO varistors has been investigated. Doping with a small amount of Nb_2O_5 worsened the electrical and pulse degradation characteristics. However, with 0.05–0.1 mol% Nb_2O_5, the electrical and pulse degradation characteristics were greatly improved, but further doping with Nb_2O_5 had little influence. Pre-sintering of Nb_2O_5 with ZnO at 1000–1100 °C greatly improved the electrical and pulse degradation characteristics.

1. Introduction

Zinc oxide varistors have an excellent voltage–current non-linear characteristic which can be expressed by

$$I = KV^{\alpha} \tag{1}$$

where K is a constant and α is a non-linear coefficient. Generally, α is above 30. It is these excellent voltage–current non-linear characteristics which enable ZnO varistors to be widely used as over-voltage protectors in circuits.

ZnO varistors are formed by sintering mixtures of semiconducting ZnO powder with small amounts of other oxide powders, such as those of bismuth, antimony, cobalt, manganese, chromium, etc., [1–3] at a given temperature. The non-linear voltage–current characteristics of ZnO varistors result from the formation of double Schottky barriers at the grain boundary caused by the bismuth-rich phase surrounding the ZnO grain and the spinel phase of $Zn_7Sb_2O_{12}$ at the grain boundary [4].

It has been reported [5] that the Nb_2O_5 dopant in the binary $ZnO–Nb_2O_5$ system can raise the conductivity of ZnO grains and react with ZnO to produce $Zn_3Nb_2O_8$ spinel phase at the grain boundaries. The $Zn_3Nb_2O_8$ spinel phases form Schottky barriers at the grain boundaries, and therefore the binary $ZnO–Nb_2O_5$ system possesses non-ohmic characteristics.

The present work investigated the influence of Nb_2O_5 dopant on the non-ohmic characteristics of a multi-component ZnO varistor composed of the oxides of bismuth, manganese, cobalt, chromium, titanium and lead.

2. Experimental procedure

2.1. Sample preparation

Nb_2O_5 was doped in two ways.

(A) Nb_2O_5 was doped directly into ZnO powder with other oxides of bismuth, manganese, cobalt, chromium, titanium and lead in specific proportions. The mixture was milled with agate balls and deionized water for 48 h. After being air-dried and sieved, the mixture was calcined at 750 °C for 1 h. The calcined mixture was ball milled for further 24 h, air-dried and sieved. Finally the discs of 8 mm diameter were pressed and sintered at 1240 °C for 2 h and furnace-cooled to room temperature. After lapping both surfaces, silver paste was coated on the surfaces by sintering at 550 °C for 15 min.

(B) ZnO and Nb_2O_5 were first mixed in specific proportions, ball-milled for 48 h, air dried and sieved. The mixture of ZnO and Nb_2O_5 was sintered at 800, 1000, 1100, and 1200 °C for 2 h, respectively. The pre-sintered mixtures of ZnO and Nb_2O_5 are mixed with other oxides of bismuth, manganese, cobalt, chromium, titanium and lead, and the above preparation process was repeated.

2.2. Electrical characterization measurement

The samples were placed in an earthed metal box. The V–I characteristics were measured using a d.c. supply and an ammeter at a fixed temperature.

3. Results

Fig. 1 shows the influence of the amount of Nb_2O_5 dopant on the V–I characteristics of ZnO varistors obtained by process A. From the V–I characteristics, the non-linear coefficient may be calculated as follows

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)} \tag{2}$$

where V_1 and V_2 are the voltages corresponding to the currents of I_1 and I_2, respectively. The non-linear coefficient and breakdown field, E, of ZnO varistors vary with Nb_2O_5 dopant as shown in Fig. 2. When the amount of Nb_2O_5 dopant is small, the non-linear

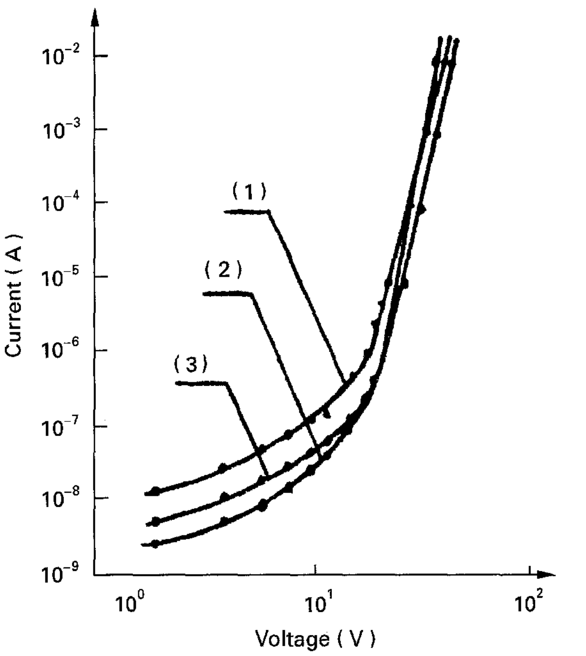

Figure 1 V–I curves of ZnO varistors obtained by process A with various Nb_2O_5 dopant levels (1) 0.05 mol%, (2) 0.1 mol%, (3) 0.2 mol%.

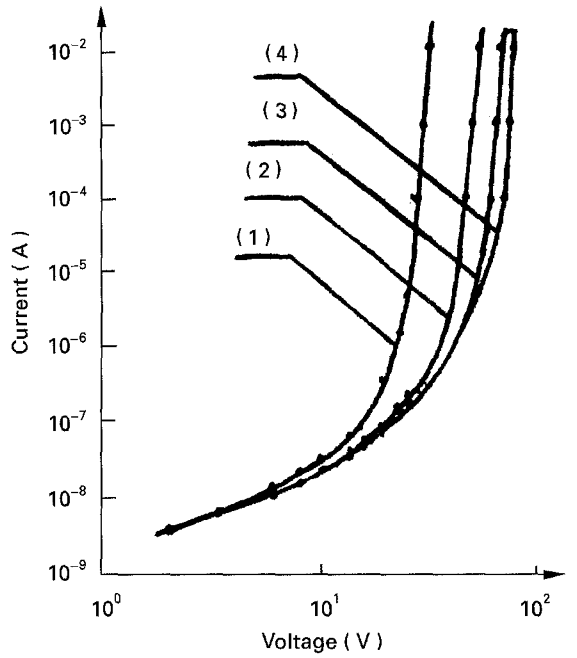

Figure 3 V–I curves of ZnO varistors at pre-sintering temperatures of (1) 800 °C, (2) 1000 °C, (3) 1100 °C, (4) 1200 °C.

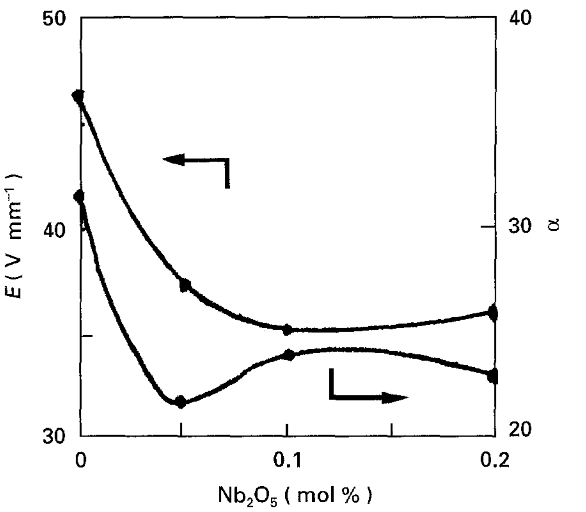

Figure 2 Influence of Nb_2O_5 dopant on breakdown fields, E, and non-linear coefficient, α, of ZnO varistors.

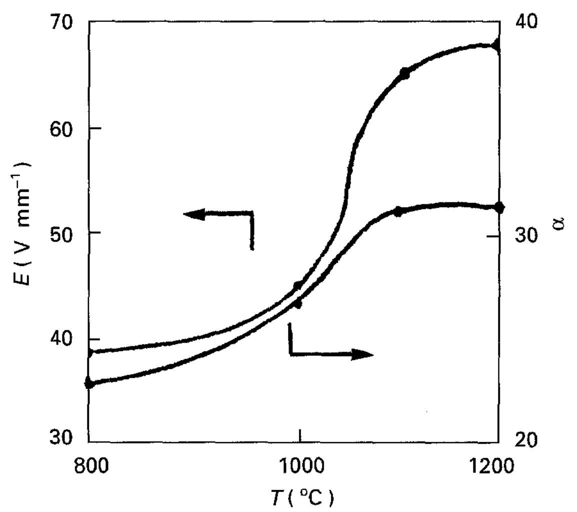

Figure 4 Breakdown field, E, and non-linear coefficient, α, versus pre-sintering temperature.

coefficient and breakdown field of ZnO varistors decrease sharply with the increase in amount of Nb_2O_5 dopant, but when the amount of Nb_2O_5 dopant exceeds 0.05 mol%, the breakdown field continues to decrease, whereas the non-linear coefficient increases. The breakdown field reaches its minimum and the non-linear coefficient its maximum when the amount of Nb_2O_5 dopant is 0.1 mol%. Thereafter, the breakdown field increases and the non-linear coefficient decreases slightly with the increase in the amount of Nb_2O_5 dopant.

The pre-sintering of Nb_2O_5 with ZnO has a profound influence on the electrical characteristics of ZnO varistors, especially the pre-sintering temperature. Fig. 3 shows the V–I characteristics of ZnO varistors corresponding to the pre-sintering temperatures of 800, 1000, 1100, and 1200 °C. The pre-sintering temperature has no influence on pre-breakdown region of the ZnO varistor. Fig. 4 shows that the non-linear coefficient and breakdown field of ZnO varistors vary with the pre-sintering temperature. It can be seen that the non-linear coefficient and breakdown field increase with increasing pre-sintering temperature.

The influence of Nb_2O_5 dopant on the pulse degradation of ZnO varistors is shown in Fig. 5. The pulse degradation characteristics of ZnO varistors are poor when the amount of Nb_2O_5 dopant is small, but are improved with increasing the amount of Nb_2O_5 dopant. However, large amounts of Nb_2O_5 dopant have little influence on the pulse degradation characteristics of ZnO varistors. Fig. 6 shows the influence of pre-sintering temperature on the pulse degradation characteristics of ZnO varistors. If can be seen that the higher the pre-sintering temperature, the better are the pulse degradation characteristics.

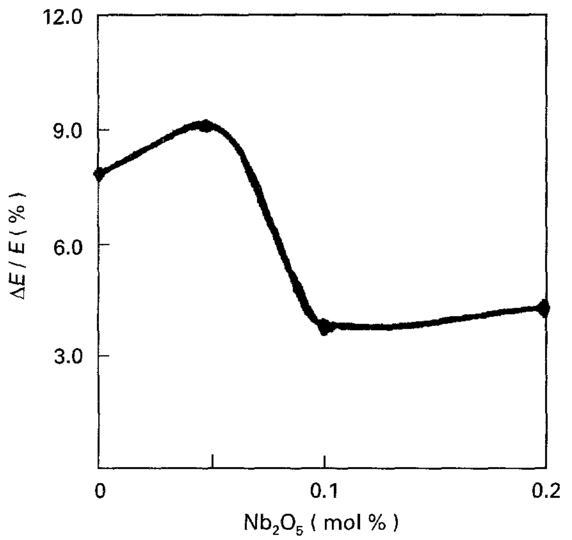

Figure 5 Pulse degradation of ZnO varistors versus Nb_2O_5 dopant.

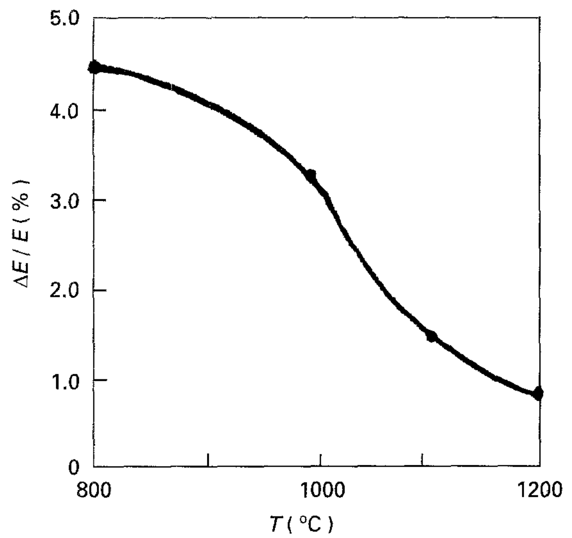

Figure 6 Pulse degradation of ZnO varistors versus pre-sintering temperatures.

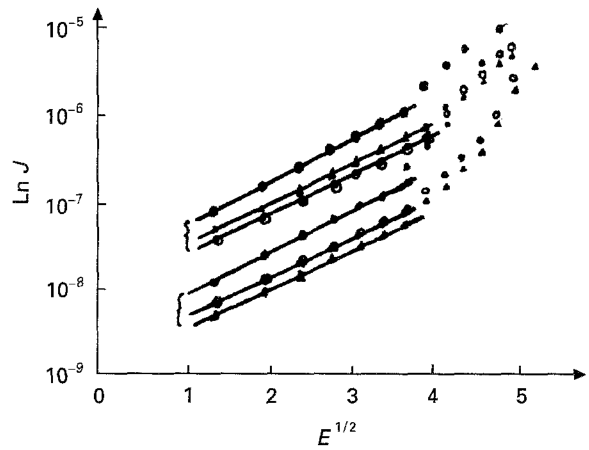

Figure 7 J–E plot with Nb_2O_5 dopant levels of (●) 0.05, (▲) 0.1 and (○) 0.2 mol% at 28 °C and 82 °C.

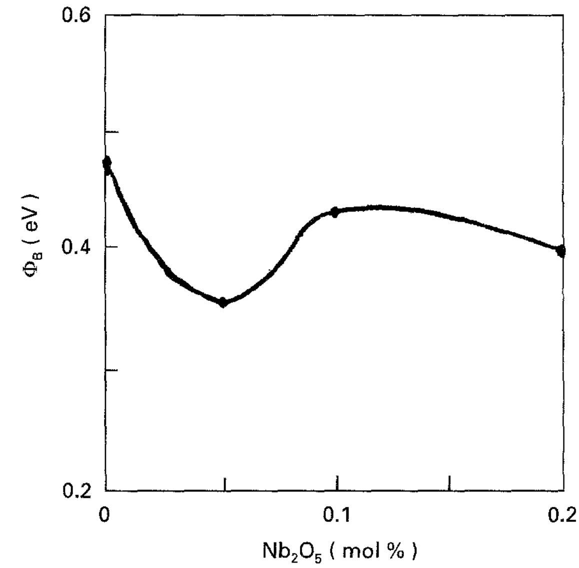

Figure 8 Barrier height versus Nb_2O_5 dopant.

4. Discussion

The non-linear characteristics of ZnO varistors are attributed to the Schottky barrier at the grain boundary. Therefore, the electrical characteristics and pulse degradation should be related to the Schottky barrier at the grain boundary. In the pre-breakdown region, the V–I characteristics are expressed as [6],

$$J = J_0 \exp\left(\frac{\Phi_B - \beta E^{1/2}}{kT}\right) \quad (3)$$

where Φ_B is the Schottky barrier height, E the electrical field, J the current density, and J_0 and β are constants. Different barrier heights produce different V–I characteristics.

From Equation 3, we obtain

$$\ln J = \ln J_0 + \frac{\Phi_B}{kT} - \frac{\beta}{kT} E^{1/2} \quad (4)$$

Equation 4 shows that the relationship between $\ln J$ and $E^{1/2}$ is linear at a definite temperature in the pre-breakdown region. Therefore, we can obtain the barrier height, Φ_B, from the intercept of the $\ln J$ and $E^{1/2}$ plot at different temperatures.

Fig. 7 shows the linear relationship between $\ln J$ and $E^{1/2}$ with different amounts of Nb_2O_5 dopant at 28 and 82 °C, respectively. From the intercept, the barrier height, Φ_B, corresponding to different amounts of Nb_2O_5 dopant can be obtained as shown in Fig. 8. Because the amount of Nb_2O_5 dopant is small, Nb_2O_5 doping makes the barrier height, Φ_B, decrease. When the amount of Nb_2O_5 dopant is between 0.05 and 0.1 mol%, the Schottky barrier height, Φ_B, increases with the increase in the amount of dopant. The Schottky barrier height, Φ_B, decreases again as the amount of Nb_2O_5 dopant exceeds 0.1 mol%.

Because the ionic radii of Nb^{5+} and Zn^{2+} are 0.048 and 0.060 nm [7], respectively, Nb^{5+} will occupy the Zn^{2+} sites in the depletion layer at the grain boundary as the amount of Nb_2O_5 dopant is below 0.05 mol%. Thus, the following reactions occur

$$Nb_2O_5 \overset{ZnO}{\rightleftharpoons} 2Nb_{Zn} + 2O^0 + 3/2O_2(g) \quad (5)$$

$$Nb_{Zn} \rightleftharpoons Nb_{Zn}^{3\circ} + 3e' \quad (6)$$

Reactions 5 and 6 show that the doping of Nb_2O_5 makes the donor concentration in the depletion layer at the grain boundary increase. The Schottky barrier height, Φ_B, at the grain boundary can be written as [8]

$$\Phi_B = \frac{e^2 N_s^2}{2\varepsilon\varepsilon_r N_d} \qquad (7)$$

where N_s is the surface state density, N_d the donor concentration, and ε_r the relative dielectric constant of ZnO ceramics.

The first doping makes the donor concentration, N_d, increase, resulting in a decrease of the Schottky barrier height, Φ_B. On increasing amount of Nb_2O_5 dopant from 0.05 mol%–0.1 mol%, we assume that the niobium ions will compete for the interstitial sites which will otherwise be occupied by interstitial zinc ions. At this time, niobium behaves as an acceptor

$$1/2Nb_2O_5 \rightleftharpoons Nb_i^{3'} + 3h^{\circ} + 5/4O_2(g) \qquad (8)$$

Thus the electrons generated in Reaction 6 are absorbed as a result of $Nb_i^{3'}$ formation. A similar situation for aluminium dopant in ZnO has been mentioned in the literature [9], in which aluminium acts as an acceptor in the interstitial sites in the depletion layer. This causes the donor concentration, N_d, to decrease and resulting in an increase of the Schottky barrier height. Further doping with Nb_2O_5 causes the Nb_2O_5 dopant to segregate at the grain boundary and to react with ZnO to form $Zn_3Nb_2O_8$ spinel. It is reported that the $Zn_3Nb_2O_8$ spinel possesses different electrical resistivity compared with the matrix [5]. The resistivity of $Zn_3Nb_2O_8$ spinel increases with increasing amount of Nb_2O_5 dopant. When the amount of Nb_2O_5 dopant is too great, the resistivity of spinel decreases with increasing amount of Nb_2O_5 dopant. Thus it is easy for ions to migrate at the grain boundary as the amount of Nb_2O_5 is too large. This decreases the surface state density at the grain boundary and results in a fall of the Schottky barrier height. Because the Schottky barrier height varies with Nb_2O_5, it may explain the variation of the non-linear coefficient with Nb_2O_5.

The influence of pre-sintering temperature on Schottky barrier height is shown in Fig. 9. When the pre-sintering temperature is lower than 1000 °C, no reaction occurs between ZnO and Nb_2O_5. The pre-sintering between ZnO and Nb_2O_5 helps Nb^{5+} to occupy the Zn^{2+} sites during the sintering of the mixture of ZnO and Nb_2O_5 with other oxides, and thus increases the donor concentration in the depletion layer and decreases the Schottky barrier height. When the pre-sintering temperature is higher than 1000 °C, Nb_2O_5 reacts with ZnO to form $Zn_3Nb_2O_8$ spinel. The higher the pre-sintering temperature, the stronger is the reaction between ZnO and Nb_2O_5. This will cause Nb_2O_5 to segregate preferentially at the grain boundary during the sintering of the pre-sintered mixture with other oxides. The amount of $Zn_3Nb_2O_5$ spinel formed at the grain boundary increases with increasing pre-sintering temperature. Thus the surface state density, N_s, increases with the increase of pre-sintering temperature which, in turn, raises the Schottky barrier height. As the pre-sintering temperature is higher than 1100 °C, it is possible that ZnO reacts with Nb_2O_5 completely, leading to a slight increase in surface state density. Thus the Schottky barrier height increases slightly with increasing pre-sintering temperature. This is inconsistent with the variation of the non-linear coefficient with pre-sintering temperature (Fig. 4).

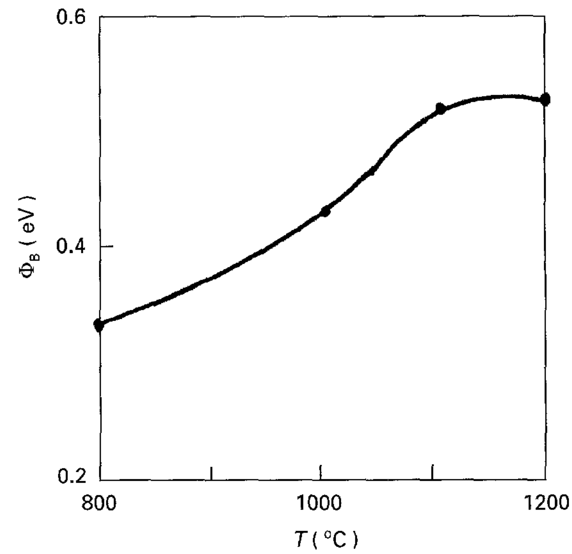

Figure 9 Barrier height versus pre-sintering temperature.

The degradation of ZnO varistor is attributed to the migration of ions at the grain boundary [10]. The migrated ions may be the interstitial zinc ions in the depletion layer [11] or the oxygen ions in the Bi_2O_3-rich intergranular layer [10]. After Nb_2O_5 is doped into ZnO, Reactions 5 and 6 occur. The electron density in the depletion layer increases greatly. Because the radius of Nb^{5+} is less than that of Zn^{2+}, the replacement of Nb^{5+} for Zn^{2+} in the zinc sites will cause the lattice to distort and make more room for interstitial zinc ions to migrate from one site to another. As the amount of Nb_2O_5 dopant increases above 0.05 mol%, niobium ions begin to occupy the interstitial sites and Reaction 8 occurs. This can decrease the amount of interstitial zinc ions. Therefore, the pulse degradation characteristics are improved. Further increase of Nb_2O_5 dopant causes Nb_2O_5 to segregate at the grain boundary and to form $Zn_3Nb_2O_8$ spinel phase. As stated above, $Zn_3Nb_2O_8$ spinel formed in the intergranular layer possesses different electrical resistivity compared with the matrix. The resistivity of $Zn_3Nb_2O_8$ spinel varies with the amount of Nb_2O_5 dopant and reaches a maximum at 0.1 mol% Nb_2O_5. High resistivity makes it difficult for ions to migrate in the intergranular layer. Thus, the first doping with Nb_2O_5 will prevent more interstitial zinc ions from migrating in the depletion layer. Further doping with Nb_2O_5 results in the segregation of Nb_2O_5 in the grain boundary and forms $Zn_3Nb_2O_8$ spinel. This will prevent the ions from migrating in the intergranular layer. Doping with too much Nb_2O_5 causes the resistivity of $Zn_3Nb_2O_5$

spinel to decrease and the ions in the intergranular layer can thus migrate easily.

The pre-sintering of Nb_2O_5 with ZnO makes the formation of $Zn_3Nb_2O_8$ easier. The increase in the amount of $Zn_3Nb_2O_8$ spinel results in an increase of the resistivity of the intergranular layer. Thus, the ions cannot migrate easily. The higher the pre-sintering temperature, the greater is the amount of $Zn_3Nb_2O_8$ spinel and the greater the resistivity of the intergranular layer. This can prevent the ions from migrating greatly and improves the degradation characterization of ZnO varistors.

5. Conclusion

Nb_2O_5 doping and pre-sintering of Nb_2O_5 with ZnO have significant influences on electrical and pulse degradation characteristics of ZnO varistors. The amount of Nb_2O_5 dopant which greatly affects the electrical and pulse degradation characteristics of the ZnO varistor, falls in the range 0–0.1 mol%. Higher pre-sintering temperature will improve the electrical and pulse degradation characterization of ZnO varistors.

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