

Boron Back Surface Field Using Spin-On Dopants by Rapid Thermal Processing

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We have studied the application of a rapid thermal processing (RTP) for boron diffusion using spin-on dopants (SODs). For the diffusion, six different p-type SODs (four with only boron, one with boron and aluminium, and one with aluminium and gallium) were used on n-type 1 Ω -cm float-zone (FZ) silicon. The sheet resistivity formed with diffused boron SODs is sufficiently low for use of back surface field (BSF) in solar cells. A sheet resistivity of under 40 Ω /Sq was obtained by using rapid thermal diffusion (RTD) at 1050 $^{\circ}$ C for 60 s. Also, a sheet resistivity of lower 20 Ω /Sq was reached at 1100 $^{\circ}$ C for 120 s. A surface concentration of $2 \sim 3 \times 10^{20}$ cm^{-3} and a junction depth of 0.5 \sim 0.6 μm were measured by electrochemical capacitance voltage (ECV). On the other hand, the sheet resistivity of BSF diffused with an aluminum (Al) and boron mixed SODs was not absolutely reliable because the measurements of the sheet resistivity were very difficult due to the crystals of Al that formed on the surface. Using a simple design, we fabricated solar cells with boron dopants as a BSF. A cell efficiency of 14.6 % on 1 Ω -cm FZ silicon with a V_{oc} of 594 mV was obtained. We assumed that the losses of efficiency and V_{oc} were caused by degradation of the bulk lifetime of the material after boron diffusion.

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I. INTRODUCTION

If high-efficiency solar cells are to be obtained, both bulk and surface recombination must be low, so various surface passivation methods have been investigated [1-4]. One effective surface passivation method is the built-in electric field at the back surface as a low-high junction which enhances not only the short-circuit current but also the open-circuit voltage of a solar cell. Widely used back surface field dopants are aluminum and boron.

The Al-dopant layer is normally evaporated or screen printed. The formation of an Al-Si alloyed layer at low temperature is a well-known advantage of the Al-back surface field (BSF). Therefore, co-diffusion of phosphorus for the emitter and Al for the BSF is possible, resulting in enhanced phosphorus diffusion due to the so-called push effect [5] and improved diffusion length in the material due to gettering, which is able to increase the bulk lifetime during the process [6]. Moreover, a reflector effect is present due to the Al alloying, and the thickness of the junction depth can be varied easily. However, rear re-

combination at the Al-Si rear contacts is relatively high because the Al concentration of the Al/Si alloy is not more than 3×10^{18} cm^{-3} [7].

On the other hand, boron is an other attractive candidate for a BSF layer. For boron diffusion, high temperatures (over 1000 $^{\circ}$ C) and long process times are necessary in order to achieve high concentrations and large junction depths. However, boron diffusion has advantages in that boron is more soluble in silicon than aluminum. Thus, the surface concentration of boron is higher than that of Al. In addition, boron diffusion yields more uniform junctions than alloying. Therefore, a boron-diffused BSF is more suitable than aluminum-alloyed BSF.

In this work, we investigated the cost effectiveness of boron diffusion by rapid thermal processing (RTP) using spin-on dopants (SODs). SODs are solutions which are deposited on semiconductor surfaces. The advantages of SOD are convenient application of the dopant, easy control of the doping concentration and the junction depth, simultaneous diffusion without a mask, and low cost. In the case of rapid thermal diffusion (RTD) high heating and cooling rates can be increased over 100 $^{\circ}$ C/s. This allows short process times in the range of a few seconds.

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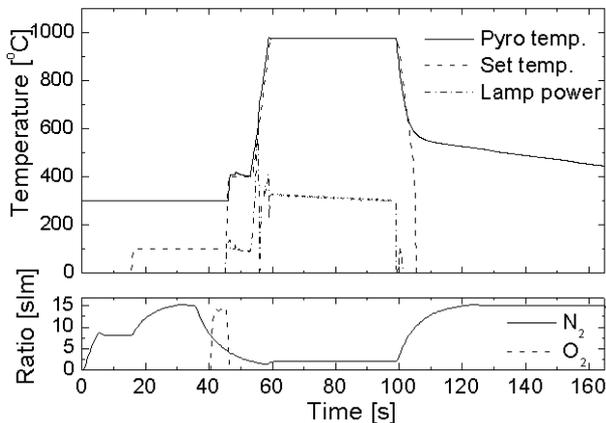


Fig. 1. Typical schematic of a rapid thermal diffusion (RTD) process. For B-diffusion, the heating and the cooling rates are fixed at $100\text{ }^{\circ}\text{C/s}$ and plateau temperature and the time are varied between $1000\text{ }^{\circ}\text{C}$ and $1100\text{ }^{\circ}\text{C}$ and between 60 s and 180 s , respectively.

In order to find the optical process for BSF in solar cells, we varied the process time and process temperature. Furthermore, the resulting diffusion samples were characterized by measuring the sheet resistivity and the concentration profiles. Lastly, phosphorus SODs as an emitter and boron SODs as a BSF were used to produce solar cells by RTP and their parameters were analyzed.

II. EXPERIMENTS

1. Experiment Procedures

In this work n-type float zone (FZ) silicon wafers with a resistivity of $1\ \Omega\text{-cm}$ and a thickness of $250\ \mu\text{m}$ were used. Four only-boron and two mixed p-type SOD sources provided by Filmtronics, as shown in Table 1 were applied for diffusion. The only-boron SODs are Boron A, B155, and B153 and B0.008 and the mixed SODs are Al/B120 and Al/Ga130. Each dopants concentration is also shown in Table 1. After RCA cleaning, the wafers were placed on a spinner and the SODs were dropped on the center of the wafer. The SOD required for a 4-inch wafer was $750\ \mu\text{l}$, and the rotation speed was 3000 rpm for 5 s , followed by 3000 rpm for 15 s . The coated wafer was baked on a hot plate at $200\text{ }^{\circ}\text{C}$ for 15 min to drive out the excess solvents. The next step was heat treatment at a high temperature by RTP to diffuse dopants into the wafer. The typical rapid thermal diffusion (RTD) process is shown in Fig. 1. The heating rate and the cooling rate were fixed to $100\text{ }^{\circ}\text{C/s}$. N_2 was used as an ambient gas for diffusion. Boron was diffused at temperatures in the range of $1000\text{ }^{\circ}\text{C}$ to $1100\text{ }^{\circ}\text{C}$ for $60\text{ }^{\circ}\text{C}$ to 180 s . After diffusion has been performed at different high temperatures, the borosilicate glass on the wafer was removed in a HF (50%) dip for $20\text{ }^{\circ}\text{C}$ to 30 min . The

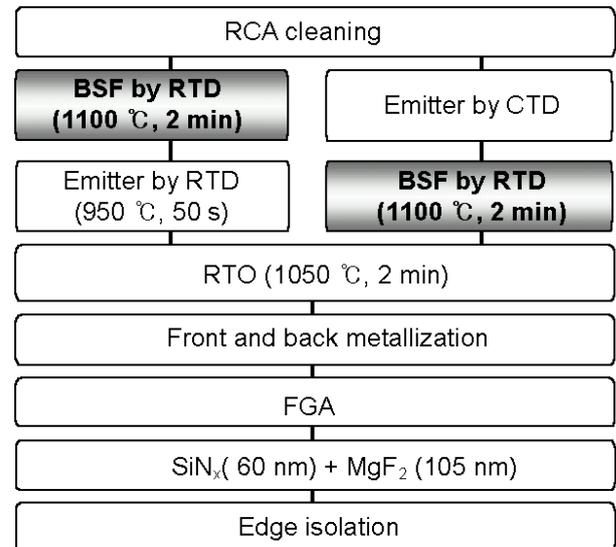


Fig. 2. Solar cell process sequence by RTP for two different cases. In the first case the B-BSF and P-emitter are diffused by RTD while in the second case the P-emitter is diffused by CTD and the B-BSF is diffused by RTD.

sheet resistivity of the doped layers was measured by using the four-point probe method. The boron profiles on n-type silicon were measured by using the electrochemical capacitance voltage (ECV) profiles.

2. Solar Cell Design and Fabrication

Simple planar solar cells, n^+pp^+ cells with planar boron BSF were fabricated. The corresponding process scheme is shown in Fig. 2. For the fabrication of solar cells, $0.5\ \Omega\text{-cm}$ p-type FZ silicon materials with a thickness of $250\ \mu\text{m}$ were used. The wafers were cleaned by using a modified RCA sequence. Two different steps for emitter were chosen. In the first, three different boron spin-on sources were deposited on the back side (on the front side 200 nm SiO_2 was deposited to prevent the diffusion of boron to the front side) and diffused at temperatures of $1100\text{ }^{\circ}\text{C}$ for 2 min . After, the borosilicate glass on the rear side and 200 nm SiO_2 on the front side were removed simultaneously. After phosphorus spin-on deposition on the front side the wafer was diffused at a temperature of $950\text{ }^{\circ}\text{C}$ for 50 s by RTP. In the second, the emitter was formed with POCl_3 diffusion by CTP, resulting in about $120\ \Omega/\square$; then, three different boron spin-on dopants were deposited on the back side. The emitter was passivated by RTO at a temperature of $1050\text{ }^{\circ}\text{C}$ for 120 s . The front contacts were formed by using photolithography and were metallized with Ti/Pd/Ag. Then, $2\ \mu\text{m}$ of Al was evaporated on to the rear side as a back contact. Finally, the solar cells were annealed at $425\text{ }^{\circ}\text{C}$ for 25 min in a forming gas.

Table 1. The four only-boron and the two mixed p-type SODs. Boron A, B155, B153 and B0.008 show the only boron SODs. Al/B120 and Al/Ga130 are mixed SODs.

Dopant concentration	Boron A	B155	B153	B0.008	Al/B120	Al/Ga130
Boron [%]	>4.0	4.0	2.0	0.008	4.0	none
Aluminium [%]	none	none	none	none	4.0	1.3
Gallium [%]	none	none	none	none	none	1.3

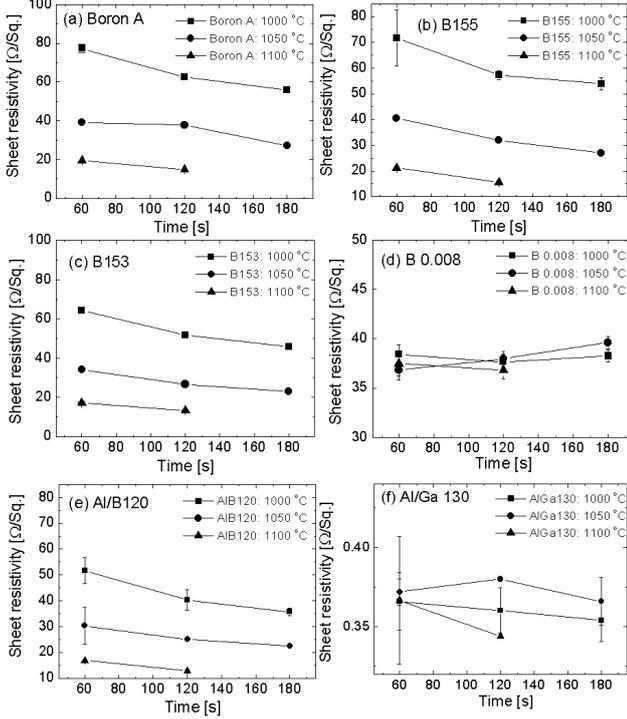


Fig. 3. Evolution of the emitter sheet resistivity with respect to the diffusion time for various diffusion temperature and time with only-boron or mixed p-type dopants.

III. RESULTS AND DISCUSSION

1. Sheet Resistivity of Boron

Figure 3 shows the dependence of the boron sheet resistivity on diffusion time and temperature for the six different p-type spin-on dopants shown in Table 1. The temperature was varied between 1000 and 1100 °C while the diffusion time was varied between 60 and 180 s.

The sheet resistivity for pure boron SODs (Boron A, B155 and B153) showed a similar trends, *i.e.*, the sheet resistivity decreased with increasing diffusion time and temperature. However, the sheet resistivity for B0.008, Al/B120, and Al/Ga130 were not absolutely reliable. The sheet resistivity of B0.008 was measured as being between 35 and 40 Ω/□, independent of the diffusion temperature and the process time. In addition, dur-

ing the measurements, the four-point device indicated not a p-type, but an n-type, material. We assume that the boron layer on the n-type material was very shallow due to the extremely low boron concentration (0.008 %); thus, during the measurement, the measured current also flowed over the n-type base material.

The sheet resistivity for the mixed SOD, Al/B120 showed the same tendency as those of pure-boron SODs. However, the measurement of the sheet resistivity was very difficult. The sheet resistivity could be measured only at a few positions on the wafer. On the other hand, the sheet resistivity of Al/Ga130 was measured to be very low, between 0.35 and 0.40 Ω/□, independent of the temperature and the time. The reason for this problem is assumed to be aluminum from the mixed dopants forming crystals on the surface, resulting in a disturbance of the measurement.

2. Boron profiles

Figure 4(a) shows the experimental concentration profiles of the spin-on boron dopants Boron A, B155 and B153 diffused into n-type Si at a temperature of 1100 °C for 2 min using RTP. The ECV profile measurement, which determines the electrically active atoms, was used to measure the boron concentration profile. In the case of all three boron dopants, the surface concentration was in the range of $2 \sim 3 \times 10^{20} \text{ cm}^{-3}$ while the junction depth was in the range of $0.5 \sim 0.65 \mu\text{m}$.

Figure 4(b) shows the boron profiles after three subsequent diffusion steps, RTD for BSF (boron) diffusion, RTD for emitter (phosphorus) diffusion, and RTO for passivation, at high temperatures in a fabrication of RTP solar cells. After this three subsequent diffusion steps, the surface concentration decreased from $2 \sim 3 \times 10^{20} \text{ cm}^{-3}$ to $1 \times 10^{20} \text{ cm}^{-3}$, and the junction depth increased slightly. Furthermore, the carrier concentration profile of B155 on a p-type wafer is shown in Fig. 4(b). The surface concentrations on the n- and the p-type wafers were the same, and the junction depth on the p-type wafer was $0.1 \mu\text{m}$ deeper than it was on the n-type wafer. All the boron profiles were flat near the peak region ($>10^{20} \text{ cm}^{-3}$). This is due to a higher diffusion coefficient at higher concentrations [8]. Some researchers [9–11] have reported an enhanced diffusion coefficient when using

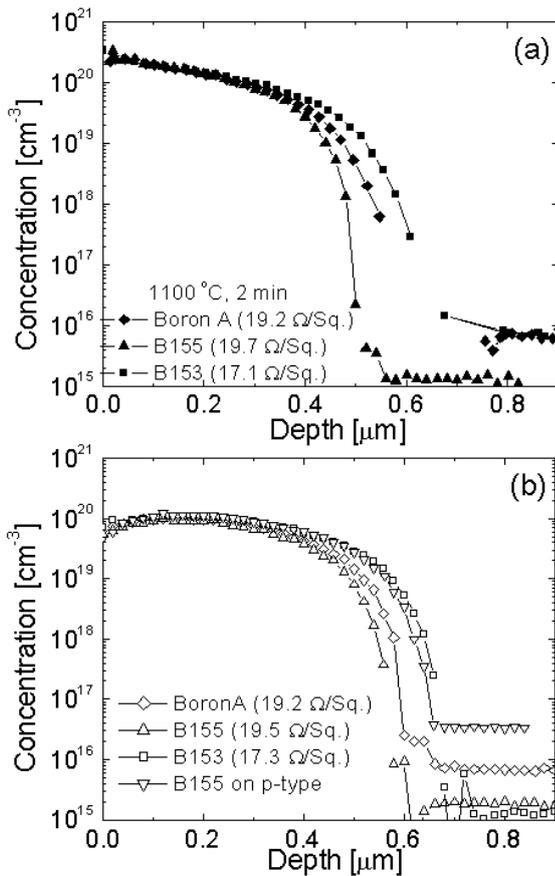


Fig. 4. Concentration profiles of three different boron SODs by ECV: (a) boron profiles on an n-type material after the RTD process at 1100 °C for 2 min, (b) boron profiles after three different subsequent RTP processes needed to fabricate solar cells: RTD for the BSF (1100 °C, 2 min) + RTD for the emitter (950 °C, 50 s) + RTO for passivation (1050 °C, 2 min).

RTP using with spin-on or ion-implanted sources.

On the other hand, the difference in the background concentrations of the doping profiles was due to side-wall effects in the ECV measurement [7] or to slight differences in the base doping concentrations of the wafers.

3. Solar Cells Fabrication

Table 2 shows a comparison of the solar cells fabricated with different methods for the emitter and the BSF. The upper three cells (No8-6, No10-6, and No12-6) are complete RTP cells, where both the emitter and the BSF were produced with spin-on dopants by RTP, whereas the lower three cells (No14-1, No15-1, and No17-6) were fabricated using classical thermal diffusion (CTD) for the emitter and RTD-BSF. Additionally, the Ref cell with a boron BSF fabricated by CTD with BBr_3 gas was used as a reference cell.

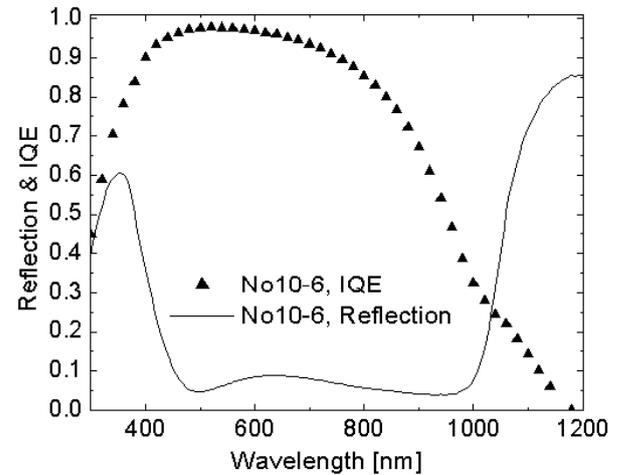


Fig. 5. Internal quantum efficiency (IQE) and reflection of solar cells.

All cells fabricated with spin-on dopants by RTP (RTD-BSF) had values of J_{sc} comparable to that of the reference cell. However, V_{oc} was lower than that of the reference cell. For example, the V_{oc} of solar cell with RTD-BSF only reached 596 mV and was reduced more than 56 mV (8.6 % relative). We assumed that the RTD-BSF not only has no effect on the passivation quality of the rear surface but also degraded the bulk lifetime in the processing. A low fill factor was only observed for some RTD cells which had an RTD emitter and had been edge-isolated by using a laser. The low FF can be assumed to be due to the laser isolation or to high emitter-metal contact resistance caused by the thin emitter. We will investigate the reason for the losses in V_{oc} which were strongly associated with the quality of passivation on the front and the rear sides of the solar cells.

Figure 5 shows the internal quantum efficiency (IQE) of the best solar cell with a boron-doped BSF. The IQE of the cell with the RTD-BSF was reduced drastically for long wavelengths (800 ~ 1000 nm), which was associated with both the bulk lifetime and the rear surface recombination velocity (S_{rear}). We could not determine whether the sharp drop in the IQE of the cells with the RTD-BSF could be attributed to a degradation in the rear surface passivation or in the bulk lifetime (τ_b).

In order to determine the bulk lifetime, we processed the same materials used in the solar cells at a temperature of 1100 °C for 2 min by RTP after the deposition of three different boron spin-on dopants. The silicon materials after the RTP process were etched about 20 μm on each side to remove the contamination on the surface and to measure the bulk lifetime. For the lifetime measurements, the samples were passivated on both sides with an excellent SiN_x passivation layer ($S < 10 \text{ cm/s}$). Therefore, the effective lifetime measured using microwave-detected photo-conductance decay (MW-PCD) can be regarded as the bulk lifetime. Fig. 6 shows

Table 2. Results of solar cells with respect to different types of emitters and back surface fields. The RTD-emitter was fabricated by using RTD with the spin-on method, and the CTD-emitter was produced by using CTD with the BBr₃ gas method. The RTO stack as an antireflective layer represents 10 nm SiO₂ + 60 nm SiN + 105 nm MgF₂.

No.	Emitter	BSF	AR layer	Isolation	V _{oc} [mV]	J _{sc} [mA/cm ²]	FF [%]	η [%]
No8-6	RTD	Boron A	RTO stack	laser	596.4	30.73	0.79	14.4
No10-6	RTD	B153	RTO stack	laser	594.2	30.58	0.80	14.6
No12-6	RTD	B155	RTO stack	laser	592	29.69	0.74	13
No14-1	CTD	Boron A	RTO stack	no	588.9	29.61	0.79	13.8
No15-1	CTD	B153	RTO stack	no	587.4	29.31	0.78	14.0
No17-6	CTD	B155	RTO stack	no	587.4	30	0.81	13.8
Ref.	CTD	B-CTD	SiO ₂ 105 nm	no	650.1	33.29	0.82	17.8

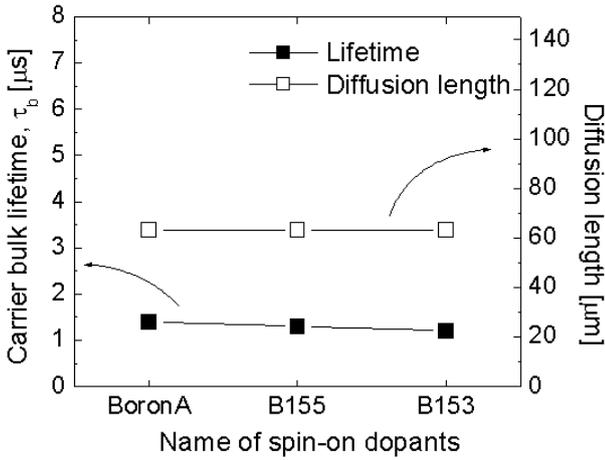


Fig. 6. Bulk lifetime and diffusion length for samples with three different boron dopants. Samples are boron-doped FZ-Si materials with a resistivity of 1 Ω -cm.

the bulk lifetime and diffusion lengths for the samples using three different dopants. The carrier lifetime of all three samples was only 1.5 μ s while the reference sample which was processed with the same steps, except for the boron dopants showed a lifetime of more than over 350 μ s. Thus, it can be concluded that boron dopants degrade the lifetime of materials.

In order to verify that the bulk lifetime of the cells with the RTP BSF was degraded, we calculated the effective diffusion lengths, L_{eff} , from the IQE responses. The bulk lifetimes of the cells with a RTP BSF were obtained in the range of 1.0 ~ 2.2 μ s. The very low L_b , less than half the cell thickness of 250 μ m, explains why boron

BSF had hardly any effect on the cell performance. It can be concluded that the bulk lifetime is severely reduced by boron diffusion using spin-on dopants. It is likely that in spite of the short process time the contamination from dopants is diffused in the bulk because of the high temperatures.

IV. CONCLUSION

We investigated the diffusion of phosphorus and boron by using two simple, cost-effective techniques, *i.e.*, spin-on dopants and rapid thermal processing. Diffusion of three different phosphorus spin-on dopants was performed in the temperature range of 850 ~ 1025 $^{\circ}$ C for 5 ~ 80 s. Diffusion of p-type dopants was performed with three pure boron SODs and three Al/B or Al/Ga mixed SODs at temperatures between 1000 and 1100 $^{\circ}$ C for 60 ~ 180 s.

The surface concentration and the junction depth strongly depended on the concentrations of spin-on dopants, the process times, and the temperatures. In the case of boron dopants, the surface concentrations were 1 ~ 3 $\times 10^{20}$ cm⁻³, and the junction depths were 0.5 ~ 0.7 μ m. In a simulation using PC-1D, the V_{oc} and the efficiency of the cells with a boron BSF with spin-on dopants should reach more than 628 mV and over 17.5 %, respectively.

Phosphorus SODs as a emitter and boron SODs as a back surface field were used to fabricate n⁺pp⁺ solar cells. Unfortunately, the RTP-BSF cells with spin-on dopants had low values of V_{oc}, less than 600 mV, while the reference cell passivated with 105 nm SiO₂ on the

rear surface had a V_{oc} of 679 mV. The main reason for the low V_{oc} was degradation of the diffusion length after boron diffusion. The diffusion lengths (L_b) of the cells with RTP BSF as obtained from the IQE were about $54 \sim 70 \mu\text{m}$ ($1 \sim 2 \mu\text{s}$) while those of the reference cell were $980 \mu\text{m}$ ($348 \mu\text{s}$). It is assumed that impurities or contamination from the boron dopants diffuse into the bulk of the silicon materials during high-temperature thermal processes, thereby reducing the bulk lifetime.

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