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NUMERICAL AND EXPERIMENTAL INVESTIGATION OF SUSTAINABLE RINSING PROCESSES FOR SILICON SOLAR CELL MANUFACTURING

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ABSTRACT: In this work, potential improvements for the rinsing process of Si wafers are identified. A numerical model was developed which describes the concentration distribution near the wafer surface of potassium hydroxide (KOH) as a function of time, temperature, volume flow, wafer size and gap distance between the wafers. The simulation results showed that a temperature increase from 25°C to 45°C reduces the KOH concentration at the wafer surface by 35%. An increase of wafer size from M2 to M12 led to an increase in rinsing time and water consumption of 10%. In contrast to constant low-flow rinsing, the combination of a phase without flow and subsequent high flow saved 35 s of process time. The simulation results were transferred to experimental rinse recipes. With regards to the flow conditions two different inlet pipes, an industrial standard and an optimized pipe are compared using three different recipes. In the experimental comparison of the rinsing scenarios, the final conductance was reduced by half for a recipe of two minutes without flow and three minutes high flow using the optimized inflow pipe, compared to the five-minute low flow recipe using the standard inflow pipe.
Keywords: Wet-chemical processes, Rinsing, Water consumption, Modelling, CFD Simulation

1 INTRODUCTION

Silicon solar cells are produced in a series of different process steps in which wet-chemical etching and rinsing steps have a considerable influence on the quality of the wafers [1,2]. The requirements for optimal flow conditions over each individual wafer surface are very high since the rinsing process must stop the reaction from the previous process step and the process solution must be rinsed off to prevent carryover into further basins. To increase the throughput in the industrial production of solar cells, wafers are processed in parallel batch processes in which two, four or six carriers with 100 wafers each are dipped in a circulated process bath. The most common method for rinsing wafers is overflow rinsing [3]. In this process, pure deionized water flows around the wafers from bottom to top in a batch process. Batch-type processes have been studied in several publications, the mass transfer and the kinetic effects [4,5], as well as the water motion [6–8]. In [9] the following adjustments were identified for water reduction during the rinse process after hydrochloric acid (HCL)-containing process: Reducing the distances between the wafers in the basin from each other (a), reducing the flow velocity of the purge flow (b), change of flow direction from upward to downward (c) and reduction of carryover of process solution (d).

For this study the concentration decrease of the process solution in a rinsing bath should be simulated to better understand the rinsing processes and thus save water in the future. A numerical model is developed which describes the concentration distribution of potassium hydroxide (KOH) as a function of temperature and volume flow at the wafer surface. Bath changes can be considered as well as the gap distance between wafers in a carrier and the wafer size. The knowledge gained from these simulations is transferred to rinsing recipes in an industrial process plant by means of experimental tests. The aim is to identify potential for improvement in the rinsing of wafers and to implement resource-saving rinsing recipes in the future.

2 APPROACH

Potential improvements for the rinsing process of Si wafers are identified regarding water consumption and rinsing times with the aim to identify potential for improvement in the rinsing of wafers and to implement resource-saving rinsing recipes in the future. During wet chemical process rinsing steps respectively rinse recipes are required to stop the reaction at the wafer surface from previous chemical process steps as saw damage edge or texturing. Since the concentration distribution directly at the wafer surface in the process basins is not accessible experimentally, the investigations are carried out by means of numerical simulation with COMSOL Multiphysics. A numerical model is developed which describes the concentration distribution of potassium hydroxide (KOH) as a function of time, temperature, volume flow and means of a bath change. With respect to larger wafer formats and higher throughputs, the effect of these larger wafer formats on the rinsing performance is investigated.

Based on the simulation results, rinsing recipe adjustments were carried out, in order to experimentally investigate at an industrial process plant. A rinsing bath of an industrial process plant consist of two inlet pipes, a perforated plate and two carriers with 100 wafer each (see Fig.1). Regarding to the flow conditions two different inlet pipes, an industrial standard pipe and an optimized pipe [10] are compared using three different recipes. The target values of the study were the measured final conductivity and the rinsing time, resulting together with the flow rate in the water consumption.

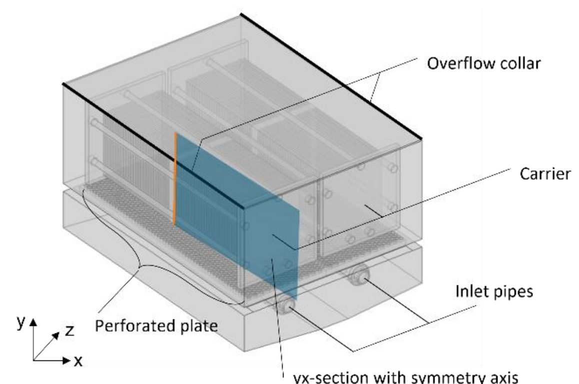

Figure 1: Industrial process basin, modified taken from [5].

3 EXPERIMENTAL SETUP

3.1 2D simulation model

In the first step a 5-wafer model is built to verify the boundary conditions for plausibility and to investigate the influence of temperature on the concentration decrease in the basin. According to the yx-section shown in Fig.1 a 100-wafer model (Fig. 2, top) is created and reduced to a 5-wafer model (Fig. 2, down). The findings are then transferred to the 100-wafer model and the effects of the number of wafers and the wafer format on the rinsing performance are observed.

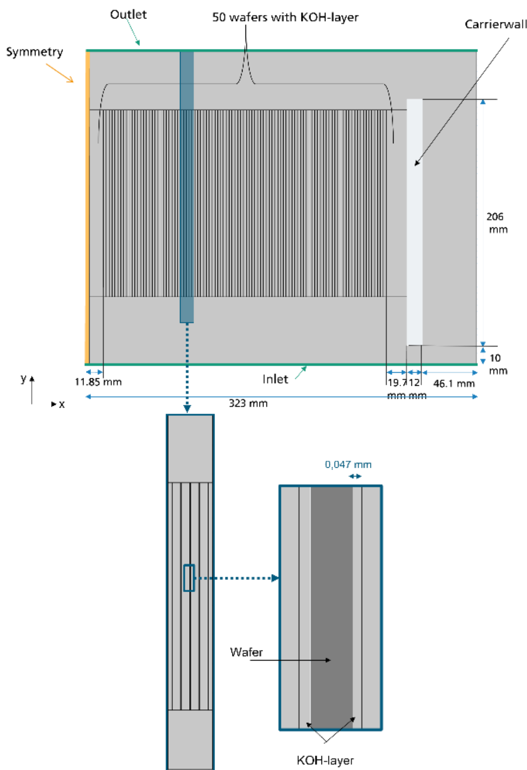

Figure 2: 100-wafer model (top), as well as the 5-wafer model (bottom left) and a detail of the 5-wafer model (bottom right).

To reduce the computational effort, the model is reduced according to its symmetry and therefore just 50 wafers must be simulated. In Fig. 1 and Fig. 2, the symmetry is marked in orange. When symmetry is chosen $v \times N = 0$, where v is the velocity field and N is the normal unit vector, it is assumed that the boundary extends indefinitely. There are no penetration conditions, and the velocity is not set to zero [11] as it is the case when the normal boundary condition is chosen. The inlet for the 100-wafer model and the 5-wafer model is the lower edge and is marked in green. Here the flow velocity is varied according to low flow (3.25 mm/s) or high flow (6.5 mm/s) conditions. The upper edge is defined as outlet, a pressure boundary condition of 0 Pa is assumed compared to the reference pressure of 1 atm. The side wall of the carrier with a thickness of 12 mm is on the right of the wafers, shown in Fig. 2. The wafers are inserted as sections with a thickness of 0.16 mm. On the left and right side of the wafers are narrow domains representing the KOH-layer with a thickness of 0.047 mm (see detail Fig.2, bottom right), carried over into the bath by the previous process step. The starting KOH concentration is assumed with 25 g/l and therefore corresponds to the concentration of the texture process. The addition of organic additives is not considered in the simulation. The area below the perforated plate (Fig. 1) is not included. A homogeneous inflow is assumed.

A laminar flow was assumed for the calculation of both, high and low flow. The Reynolds number (Re) provides information on whether a flow is laminar or turbulent. It was assumed that the rinsing process corresponds to a flow around plates, with twice the plate length as the characteristic length, the flow velocities for low and high flow and the density and viscosity of water at 20°C. With $Re_{(low\ flow)} = 1142$ and $Re_{(high\ flow)} = 2283$ are the Reynolds numbers below the critical Reynolds number $Re_c \approx 500000$ [12] for flow over a flat plate and therefore laminar flow is assumed.

To calculate mass transfer based on diffusion and convection, the transport of diluted species interface was used in addition to the laminar interface of COMSOL Multiphysics. For this purpose, the material constants and thus also the diffusion coefficient of KOH are selected with $3.7 \cdot 10^{-9}$ m²/s in the domains in which KOH is located.

The heat-transfer interface is used to map the heat exchange between the KOH-layer and the rinsing medium. It enables the calculation of heat distributions. More detailed information about the heat-transfer interface can be found in [13].

As initial value a temperature of 80°C in the KOH-layer and therefore the temperature of the alkaline texture is assumed, while the remaining domains have the initial temperature of 20°C. The calculated heat distribution is coupled with the mass transfer and flow calculation, which determines the influence of the temperature distribution on the concentration decrease in the KOH-layer.

At given KOH concentrations, the deviation of the heat transfer related material constants of KOH and the rinsing water is very small. Therefore, the thermal conductivity and capacity of water is used for the entire model. Only the heat resulting from previous alkaline texture in the KOH-layer is considered, and the stored heat in the wafer itself is neglected.

To investigate the influence of a heated rinsing water, a further calculation is carried out. However, since COMSOL specifies the diffusion coefficients for KOH and water isothermally, the coefficients must be adjusted. In this simulation a temperature in the entire domain of 45°C is specified. This means a temperature increase of 25°C and therefore an approximately doubled diffusion coefficient for KOH in water.

The 5-wafer model is locally discretized with an unstructured mesh in the inlet and outlet regions and with a structured mesh in the KOH-layer and the region between the wafers. A coarser mesh with approx. 240000 elements can be used to calculate the flow and a finer mesh with approx. $3.7 \cdot 10^6$ elements to calculate the mass transport. The number of mesh elements and thus the calculation time is increased for the calculations of the 100-wafer model.

First, the influence of the temperature is investigated using the 5-wafer model. The heat input from the texture process through the KOH-layers into the rinser is simulated. The second simulation represents the mass transfer when the total basin temperature is increased. Both calculations are performed without a laminar flow for 60 s.

Furthermore, the influence of the wafer gab distance as number of wafers in the rinsing bath over 100 s is investigated. For this purpose, the width of the wafer gap and the number of wafers is varied using low flow conditions.

- 50 wafers with a gap width of 9.70 mm
- 100 wafers with a gap width of 4.76 mm
- 200 wafers with a gap width of 2.20 mm

In addition, the effect of the wafer format on the rinsing performance was investigated. For this purpose, the two wafer formats M2 and M12 were simulated with a low flow rate for 100 s.

To investigate the influence of different rinsing steps, the following recipes are simulated with the 100-wafer model:

Simulated recipes		
(I)	(II)	(III)
60 s low flow	60 s no flow	30 s no flow
Bath change	Bath change	30 s high flow
400 s low flow	340 s low flow	Bath change
	60 s high flow	50 s no flow
		50 s high flow
		50 s no flow
		50 s high flow
		50 s no flow
		50 s high flow
		50 s no flow
		50 s high flow

Figure 3: Three different simulated recipes with 460 s rinsing time each.

The bath change after one minute represents the quick dump process and allows a significant increase in the concentration decrease, as the wafers again enter a clean environment with a higher concentration gradient. Previous simulations showed that the KOH-layer remains near the wafer surface during rinsing and does not diffuse far into the wafer gap. Therefore, a large part of the rinse water passes through the wafer gap without KOH loading. It is also known from the simulations that in the initial phase the strength of the rinsing flow does not influence the decrease of the concentration in the KOH-layer. Therefore, the modified recipes include phases during which there is no flow in the basin, so that KOH diffuses towards the center of the wafer gap. Subsequent high-flow phases are intended to ensure faster removal of KOH.

All flow simulations are calculated stationary, the solution is transferred to the mass transport simulation, which is calculated time dependent. In the first seconds the calculation is done in steps of 0.1 s and from the first seconds on in steps of 1 s. For evaluation, the mean KOH concentration in the layers of the middle wafer is examined over time.

2.2 Experiments

Based on the numerical results, rinse recipe adjustments will be carried out, which will be experimentally investigated at an industrial process plant. Two different inlet pipes, an industrial standard pipe and an optimized pipe [10] regarding to the flow conditions are compared using three different recipes, see Fig. 3.

Experimental recipes		
(i)	(ii)	(iii)
300 s low flow	120 s no flow	60 s bubbling
	180 s high flow	180 s high flow

Figure 5: Three different experimental recipes.

A process basin is filled with 25 g/l KOH, two carriers loaded with 100 multicrystalline wafers are placed in the basin for five minutes. Afterwards the carriers are placed in the rinse. The recipes shown in Fig.3 are carried out and repeated three times. The final conductivity and the rinsing time are measured, resulting together with the flow rate in the water consumption.

3 Results

3.1 2D simulation results

In Fig. 5 the temperature in the 5-wafer model is shown. The initial temperature of the rinsing water is 20°C (purple) and the initial temperature of the KOH-layer is 80°C (white), shown in the cutout after 0.1 seconds. The temperature difference after five seconds is 3°C.

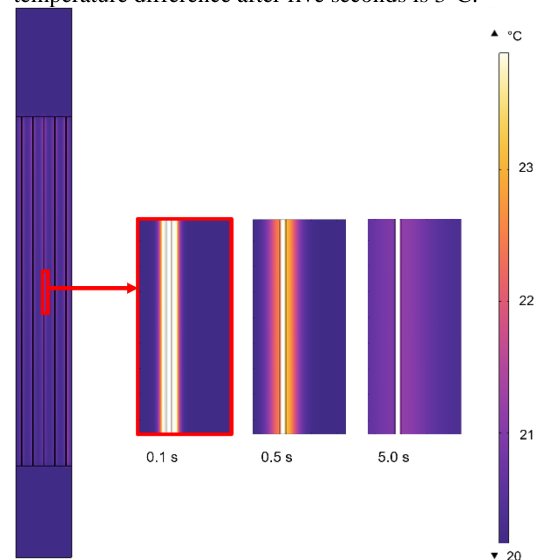

Figure 4: Simulated time dependent heat distribution from KOH-layer (left) and details on the middle wafer at seconds 0.1, 0.5 and 5 (from left to right).

It can be concluded that the influence of the temperature on the mass transport can only have a decisive influence in the initial period. At the beginning of the simulations, the diffusive mass transport dominates, and the flow does not contribute to the concentration decrease in the KOH-layer. Therefore, the influence of the temperature distribution on the flow is neglected and not further investigated.

Fig. 6 shows the result of the simulated decrease in KOH concentration after 20 s at a rinse water temperature of 45°C and 20°C.

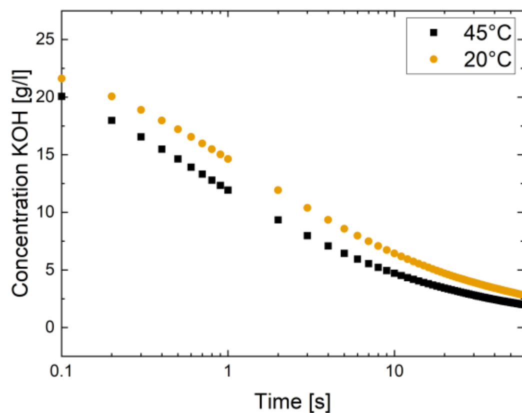

Figure 6: Simulated comparison of the decrease in KOH concentration near the wafer surface at a rinse water and KOH-layer temperature of 45°C and 20°C without flow in the first 60 seconds.

Both concentrations curves are based on diffusion processes since the simulation was carried out without flow. The figure shows a faster decrease in concentration at a water temperature of 45°C with an average concentration reduction by 35%.

Doubling the number of wafers from 100 (orange) to 200 (blue) in a process basin showed no significant effect on the concentration at the wafer surface during rinsing, as shown in Fig 7.

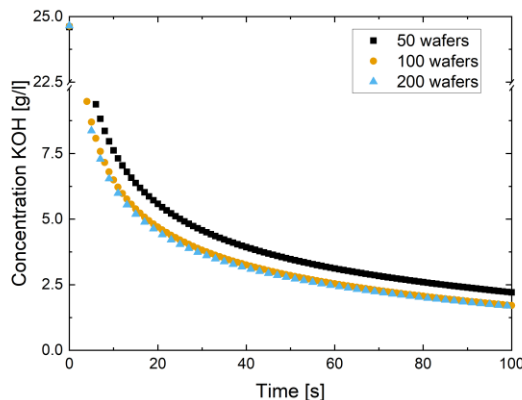

Figure 7: Simulated concentration near the wafer surface with different number of wafers per carrier, 200 wafer (blue), 100 wafer (orange) and 50 wafer (black) at low flow condition.

Although 50 wafers bring less KOH into the bath, and the flow resistance caused by the number of wafers is the lowest, the curve with 50 wafers shows a poorer decrease in the concentration. This is due to the laminar flow profile in the wafer gap for 50, 100 and 200 wafers, which decreases according to the number of wafers and the KOH diffusion near the wafer surface. The maximum flow velocity decreases as the number of wafers increases. Fig. 8 shows the flow velocities for 50, 100 and 200 wafers in the wafer gap near the wafer surface on the left y-axis. Also, the local concentration at 0 and 50 s near the wafer surface is shown on the right y-axis. The mass transport simulation is based on KOH diffusion without flow and is independent of the carrier loading. At t=0 s (green, closed symbols) the entire amount of KOH is within 0.05 mm from the wafer surface. After 50 s (green, open symbols), the diffusion of KOH concentration is within 0.7 mm from the wafer surface.

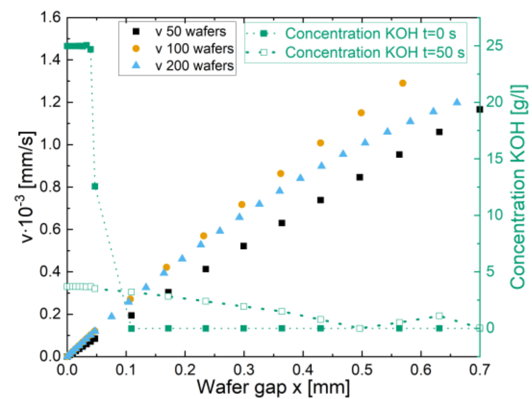

Figure 8: Simulated flow velocity v in mm/s for 50 (black), 100 (orange) and 200 (blue) wafers at low flow conditions and the KOH concentration in g/l due to diffusion without flow after 0 and 50 seconds over the wafer gap x in mm. The wafer is located at x=0 mm.

Within this marginal area, the velocity (v) for 200 wafers (blue) and 100 wafers (orange) increases more steeply than for 50 wafers (black). The velocity increase for 200 wafers is lower from x=0.35 mm compared to the 100 wafers curve since the wafer gap is significantly narrower for 200 wafers and the maximum of the laminar flow profile is therefore closer to the wafer surface. Because most of the KOH is within the first 0.4 mm, the lower curve of 200 wafers and its lower velocity has no effect on the decrease in concentration in the KOH-layer over the time. The higher velocities of the 200 and 100 wafer curves in the area between $0 < x > 0.3$ mm are decisive for the better concentration decrease. When doubling the number of wafers from 100 to 200 wafers in the basin, the concentration decreases in the KOH-layer directly at the wafer surface remains unchanged. This would allow an increase in throughput by a factor of 2, while the rinsing result, water consumption and rinsing time remain constant.

When comparing the two wafer formats M2 and M12, the wafer gaps remain the same for both simulations. After 100 s rinsing time, the average concentration for M12 with a value of 1.94 g/l KOH is just 10 % above the value for M2 with 1.77 g/l. While the diffusive mass transport of both calculations is the same, the convective mass transport in relation to the wafer surface is lower for the larger format.

When comparing the three simulated rinsing recipes, the water consumption is the same, because the increased water consumption during high flow phases is compensated by the phases without flow. The final value of the average KOH concentration for recipe (II) is 24.5% below recipe (I), see Fig. 9. The final concentration of recipe (III) is below the concentration of recipe (I) and (II). The final concentration of rinsing recipe (I) is reached 35 s earlier with recipe (III). Due to the change from no flow to high flow every 50 s the curve has a slight oscillatory shape. The final value of the average KOH concentration for recipe (III) is at least 73 % below recipe (I).

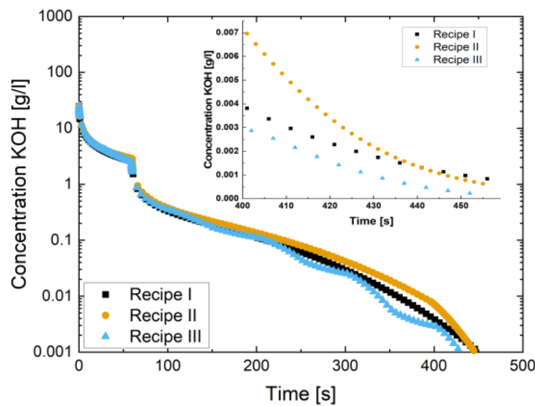

Figure 9: Simulated mean KOH concentration near the wafer surface of the 100-wafer model over rinsing time for three different recipes in the time range 0-460 s and detailed 400-460 s.

3.2 Experiments results

The simulations showed that the KOH-layer remains near the wafer surface during rinsing and does not diffuse far into the wafer gap, hence a large part of the rinse water passes through the wafer gap without KOH loading. Therefore, a recipe without flow is investigated.

In the experimental comparison of the rinsing scenarios, the optimized pipe showed an improvement in terms of rinsing performance since the final mean conductivity is below the results of the standard pipe, see Fig.10. For all three recipes the accumulated water consumption is 300 L.

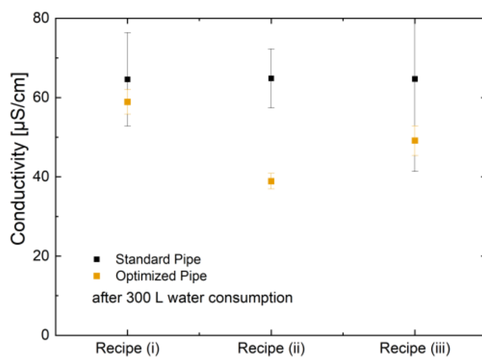

Figure 10: Mean final conductivity and standard deviation (n=3) for different recipes with standard pipe (black) and optimized pipe (orange) after 300 L of water consumption.

Compared to the standard pipe, the results of the optimized pipe also show the lower variance in the final conductivity for all recipes, resulting in more reproducible rinsing results. The final conductivity was reduced by half for recipe (ii) and the optimized inflow pipe, compared to the five-minute low flow recipe (i) and the standard inflow pipe. Recipe (ii) shows the lowest variance in the final conductivity. Therefore, the conductivity for recipe (ii) over the accumulated water consumption is shown in Fig. 11 for the standard (black) and optimized pipe (orange). In each case, the mean value with the standard deviation is shown as error band.

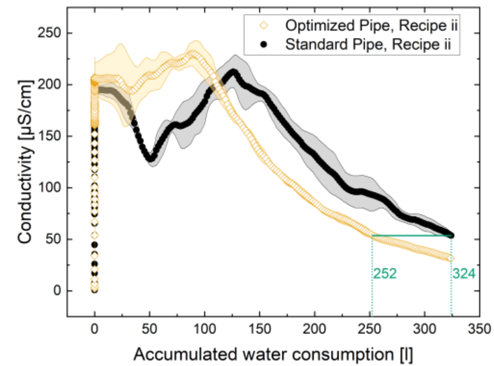

Figure 11: Conductivity and standard deviation (n=3) for recipe ii over the accumulated water consumption. At approx. 54 µS/cm the water consumption of the optimized pipe (black) is 252 l and 324 l of the standard pipe resulting in a water reduction of 72 l.

A lower standard deviation is shown within the experiments with the optimized pipe. At the end of the experiments, the curve of the standard pipe is above that of the optimized pipe. If the final conductivity value of the standard pipe is used for this recipe, the optimized pipe saves 72 l of water per run compared to the standard pipe, which corresponds to a water saving of approx. 25% per run.

4 CONCLUSION

With the use of flow simulations, it is possible to gain a deeper understanding of the rinsing processes. A temperature of 45°C reduces the average KOH concentration at the wafer surface by 35% compared to 25°C. No significant decrease in the removal of KOH near the wafer surface is found by doubling the number of wafers from 100 to 200 wafers. Larger wafer formats do not pose major challenges in terms of rinsing effects. To optimize the rinsing recipes for a sustainable rinsing, it is important to allow diffusion of KOH into the wafer gap; periods without rinsing flow are ideal for this purpose. In the experimental comparison of the rinsing scenarios, the final conductivity was reduced by half for a recipe of two minutes without flow and three minutes high flow using the optimized inflow pipe, compared to the five-minute low flow recipe using the standard inflow pipe.

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REFERENCES

1. N. Johan, M. Mohamad Shahimin, and S. Shaari, IEEE Student Conference on Research and Development (SCOReD) (2010).
2. W. Kern, ed., *Handbook of semiconductor wafer cleaning technology* (Noyes Publications, Park Ridge, N.J, 1993).

3. C.-Y. Chen, B. Panigrahi, K.-S. Chong, W.-H. Li, Y.-L. Liu, and T.-Y. Lu, J. Fluids Eng. **140**, 199 (2018).
4. M. S. Kulkarni and H. F. Erk, J. Electrochem. Soc. **147**, 176 (2000).
5. L. Mohr, T. Dannenberg, A. Moldovan, M. Zimmer, and C. Müller, Ind. Eng. Chem. Res., 17680 (2020).
6. H. Habuka, S. Kobayashi, M. Kato, T. Takeuchi, and M. Aihara, J. Electrochem. Soc. **151** (2004).
7. S. Singhal, B. Elkhatib, J. Stuber, S. V. Sreenivasan, and O. A. Ezekoye, IEEE Trans. Semicond. Manufact. **22**, 399 (2009).
8. L. Mohr, T. Krick, M. Zimmer, T. Röder, and C. Müller, IEEE Trans. Semicond. Manufact. **32**, 334 (2019).
9. O. Raccurt, F. Tardif, L. Kerber, T. Lardin, and T. Vareine, Journal of Micromechanics and Microengineering **13**, 442 (2003).
10. L. Mohr, *Numerische und experimentelle Untersuchung der Strömung sowie der chemischen Reaktionen in einem Prozessbecken für die Herstellung von Silizium-Solarzellen*. Dissertation, ISBN 978-3-8396-1764-9 (2021).
11. COMSOL 5.4, ed., *CFD Module User's Guide* (2018).
12. C. P. Kothandaraman, *Fundamentals of heat and mass transfer*, Rev. 3. ed. (New Age International (P) Ltd., Publishers, New Delhi, 2006).
13. COMSOL 5.2a, ed., *COMSOL Multiphysics 5.2*, COMSOL Reference Manual (2016).