Maintaining a Stable Etch Selectivity between Silicon Nitride and Silicon Dioxide in a Hot Phosphoric Acid Bath

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Phosphoric acid (H_3PO_4) - water (H_2O) mixtures at high temperature have been used for many years to etch silicon nitride (Si_3N_4) selective to silicon dioxide (SiO_2) layers. The production requires removing the Si_3N_4 completely while keeping SiO_2 loss to a minimum. The challenge for batch wafer cleaning is how to maintain a high etching selectivity of Si_3N_4 to SiO_2 for a longer bath life.

Experiments showed that increasing water concentration in the bath results in higher selectivity: more Si_3N_4 etched and less SiO_2 etched. With the installations of a water concentration monitor and a water spiking apparatus, the bath is able to control the water concentration. The partial replacement of the chemical bath after each product lot reduces dissolved silicon concentration. The addition of H_2SO_4 saves initial conditioning time. With all of the efforts, the bath starts at a high selectivity and maintain this selectivity for an extended bath life.

Introduction

Commonly for wet batch cleaning, Si_3N_4 is removed in a hot H_3PO_4 bath. This was used primarily for the removal of the local oxidation mask (LOCOS) that had SiO_2 underneath it for a stress relieving layer. Selectivities of 40:1 were routinely obtained and that was sufficient for that process. Today shallow trench isolation is more commonly the application, where the Si_3N_4 layer is used as the CMP (chemical mechanical planarization) stopping layer. CMP is used to remove the topography of the wafer at this step and the Si_3N_4 layer must be removed after the process. SiO_2 layers are exposed at this point and minimizing the SiO_2 loss of these layers is critical. Consequently the etch rate of the SiO_2 layers must be suppressed, raising selectivity of the Si_3N_4 to SiO_2 etch rate. This has created a need for a high selectivity silicon nitride etch processes.

In current production, the Si_3N_4 is etched out in a hot H_3PO_4 bath. Due to the limitation of SiO_2 budget on the product wafers, Si_3N_4 etching in hot H_3PO_4 intends to remove Si_3N_4 completely with minimal SiO_2 loss, and therefore, a high selectivity is desirable. Both Si_3N_4 and SiO_2 etching rates become lower and lower as production continues because of H_3PO_4's decay. In our experimental tests, for example, both Si_3N_4 and SiO_2 rates drop from 68 and 1.4 Å/minute to 40 and zero Å/minute, respectively, through the life of a H_3PO_4 bath, and consequently, the selectivity changes from 50:1 (=

68/1.4) to infinity (= 40/0) accordingly. Because SiO_2 etching rate is small and the rate is the denominator in the selectivity calculation, a small drop in SiO_2 etching rate substantially increases the selectivity value. Therefore, the control of a stable SiO_2 etching rate is very important in order to maintain a stable selectivity. The SiO_2 could change from an etching process to a deposition process, as the dissolved Si etching byproduct increases high enough in the bath. It was observed that the SiO_2 deposition starts on local areas of the wafers as soon as the etching selectivity reaches 800:1. The end of bath life is determined by either too low Si_3N_4 etching rate or the beginning of SiO_2 deposition, necessitating H_3PO_4 replacement.

In this study, targeted control of selectivity was set from 150:1 as the lower limit to 800:1 as the upper limit, where the Si_3N_4 and SiO_2 etching rates are around 53.3 and 0.35 Å/minute to 53.0 to 0.07 Å/minute, accordingly. The range between the limits is actually very narrow, in terms of how easy it is to go beyond the range in production. Consequently etching three product lots, for example, makes the selectivity change from 150:1 to higher than 800:1. Therefore, selectivity was purposely reduced immediately after each product lot was etched.

It was reported that water content in the bath impacts Si_3N_4 etching rate [1,2]. Our experiment showed that the water impacts SiO_2 etching rate as well. Understanding the chemical reactions happening in the Si_3N_4 etching is the key for achieving a desired selectivity. Equation 1 describes the Si_3N_4 etching mechanism [3,4], in which Si_3N_4, H_3PO_4 and H_2O are the reactants and $(NH_4)_3PO_4$ (phosphoric ammonium) and SiO_2 are the products. The equation indicates that increasing H_3PO_4 or H_2O accelerates Si_3N_4 etching, and reducing $(NH_4)_3PO_4$ or SiO_2 accelerates Si_3N_4 etching as well.

$$3Si_3N_4 + 4H_3PO_4 + 18H_2O = 4(NH_4)_3PO_4 + 9SiO_2 \qquad [1]$$

$$SiO_2 + 4H^+ + 4e^- = Si + 2H_2O \qquad [2]$$

Equation 1, however, does not describe the SiO_2 etching in the bath. So, we introduced equation 2. Equation 2 describes the SiO_2 etching mechanism. It is an half-reaction of SiO_2 reduction with –0.86 volts of standard reduction potential and another half is hypo-phosphoric acid ($H_4P_2O_6$) oxidation with –0.933 volts of standard reduction potential. Equation 2 expresses the correlations between SiO_2 etching and water content [H_2O], silicon concentration [Si] or acid concentration [H^+] in the H_3PO_4 bath. The [H^+] in the equation represents hydrogen ion concentration. The hydrogen ions come from the decomposition of molecules of H_3PO_4 (ortho-phosphoric acid), $H_2PO_4^-$ (dihydrogen phosphate anion) and HPO_4^{2-} (hydrogen phosphate anion). This equation shows that increasing H_3PO_4 concentration speeds up SiO_2 etching and increasing H_2O concentration or Si concentration slows down the SiO_2 etching. Our experimental results are in good agreement with the correlations. In our experiments, for example, adding fresh H_3PO_4 into the bath increased the SiO_2 etching rate, adding H_2O decreased the SiO_2 etching rate, and increasing Si concentration by etching more Si_3N_4 wafers decreased the SiO_2 etching rate.

The water is over heated at 165°C in the bath. A stable water concentration in the bath is a result of dynamic balancing between the vapor pressure generated by the water boiling out of the chemical and the pressure supplied by the lid of the bath to keep the water vapor inside the bath. We observed that the water concentration dropped quickly by just opening the lid of the bath for a few minutes. The water concentration must be controlled. Therefore, we implemented a NIR spectrometer (near infrared spectrometry) for monitoring the water concentration and implemented a de-ionized (DI) water spiking apparatus for supplying DI water into the bath at programmed intervals. With the supports of NIR spectrometer and DI water spiking apparatus, we were able to choose a water concentration and to maintain that concentration.

We observed that silicon concentration (Si) was increased in the bath simply by etching more Si_3N_4 wafers or even by etching more bare Si wafers. The increase is potentially the cause of SiO_2 deposition. In order to control Si concentration, we implemented an apparatus called: "feeding and bleeding". The apparatus automatically replenishes certain amount of chemical into the bath and drains the same amount of fresh H_3PO_4 out of the bath after each run of product lots. By doing so, the bath stabilized the Si concentration.

As explained earlier, the production is required to reduce the loss of SiO_2 in the H_3PO_4 bath due to advanced devices' lower oxide budgets. Therefore, a fresh H_3PO_4 bath needs to be conditioned by etching sacrificial nitride wafers, or by mixing with H_2SO_4 [5]. We added an amount of H_2SO_4 into fresh H_3PO_4 bath. The addition of H_2SO_4 prevents SiO_2 from its fast etching with fresh H_3PO_4. The reason is that H_2SO_4 is a stronger oxidant and it suppresses the SiO_2 etching in the bath.

Experimental Setup

Experimental testing was done in Akrion's GAMA batch tool. The tool's H_3PO_4 bath was filled with standard H_3PO_4 solution, made of 85% H_3PO_4 and 15% H_2O in weight. (All concentrations of H_3PO_4 and H_2O herein listed are weight%.) Its specific gravity is 1.69. The bath was equipped with coil cooling tubes above the chemical surface and was covered with a lid during the Si_3N_4 etching. The bath was heated up to a temperature and that temperature was maintained by a PID controlled heater. All of wafers were etched under the conditions of 165°C for 20 minutes followed by DI water rinsing and then by IPA vapor drying in other bathes, unless, their experimental conditions are specifically addressed in this article.

A NIR spectrometer was used to detect the water content. It detects water content by light absorption through the liquid. A DI water spiking apparatus was installed in the bath. The apparatus was spiking a certain amount of DI water routinely into the bath. for example, it spiked DI water for 14 seconds in every two-minute period, programmed in the tool's parameter settings. The DI water spiking rate was fixed at 60ml/minute.

Another apparatus was equipped in the bath, "feeding and bleeding". The feeding and bleeding apparatus is capable of replenishing a certain amount of fresh H_3PO_4 into the

bath and draining the same amount out of the bath automatically after each production lot etched. The feeding and bleeding apparatus replaces the chemical and reduces dissolved Si concentration. A certain amount of H_2SO_4 was also added into the fresh H_3PO_4 bath to reduce the initial SiO_2 etching rate.

200mm Si_3N_4 and SiO_2 wafers were used. The Si_3N_4 wafers had 5 KÅ thickness of Si_3N_4 film on both sides and they were used for etching rate evaluations and for the simulation of product lots. One product lot equals 1500 Å Si_3N_4 removal on both sides of 50 of the wafers. The SiO_2 wafers had 200Å SiO_2 film on both sides. The Si_3N_4 and SiO_2 films were measured with 49 points and 5 mm edge exclusion by a Rudolph S300 elipsometer. Its repeating error at one point is below 1.0 Å for the Si_3N_4 and below 0.5 Å for the SiO_2. Chemical samples were collected from the bath at tests and the elemental Si concentration was analyzed by an ICP-MS (inductively coupled plasma mass spectrometry).

Results and Discussion

Water content impacts Si_3N_4 etching rate and the correlation is described in equation 1. Figure 1 shows Si_3N_4 etching rate with four durations of DI water spiking every two-minutes. Each Si_3N_4 etching rate was evaluated after the water concentration was stabilized with the spiking. The figure shows the Si_3N_4 etching rates were 46.4, 53.4, 56.9 and 68.2 Å/minute for 5, 8, 10 and 14 seconds/two-minutes of the DI water spiking, respectively. Si_3N_4 etching rate was increased gradually with increase of the spiking duration. The spiked volumes were 5, 8, 10 and 14ml for the 5, 8, 10 and 14 seconds, respectively, because the DI water flow rate was at 60ml/minute.

Water content impacts SiO_2 etching rate as well as Si_3N_4 etching rate. Figure 2 depicts both etching rates of Si_3N_4 and SiO_2 with the change of water concentration in the same bath as for the tests shown in figure 1. The water concentrations of 3, 7.8, 10 and 14% in the bath were achieved with the spikes of 5, 8, 10 and 14 seconds per two-minutes, respectively. Figure 2(a) shows that Si_3N_4 etching rate was increased from 46.4 to 68.2 Å/minute with the change of water concentration from 3 to 14%, respectively. Figure 2(b) shows that SiO_2 etching rate was decreased from 2.12 to 1.42 Å/minute with the change of water concentration from 3% to 14%, respectively.

Reduction of water content was detected as soon as the fresh bath was heated up. The reduction went faster after the bath's temperature reached above water's boiling point. The water content could come down as low as 3% from its original 15% after the lid was opened for a long period at 165^oC. Stable water concentration was achieved at a temperature after the equilibrium reached between the water evaporating and the water spiking. Figure 3 gives an example of the water stabilization with a routine DI water spike at 165^oC. The water content was monitored by a NIR spectrometer. In this example, the water concentration reached 13.5% from 8%, after three hours of balancing between water evaporating and the spiking and then it stayed at 13.5% with ±0.1% variation.

Figure 4 shows the stabilized water concentration at different temperatures.   It shows that the water concentration was stabilized at 17.7, 16.6, 15.4 and 14.0% at 150, 155, 160 and 165°C, respectively, with 14 seconds /two-minutes of DI water spike. The bath had a higher water concentration at a lower temperature.

Etching Si_3N_4 wafers or bare Si wafers produces Si in the bath. The increase of dissolved Si concentration slows down SiO_2 etching as well as the Si_3N_4 etching. SiO_2's slowing down causes the change of selectivity more significantly than the Si_3N_4's slowing down, resulting in increased selectivity. Figure 5 illustrates the selectivity increase by etching one product lot (50 Si_3N_4 wafers) followed from etching one lot of Si dummy wafers at 165°C with 14 seconds / two-minutes of DI water spike. The bath started with 325:1 selectivity. The selectivity was increased to 489:1 from 325:1 by etching one product lot and then was further increased to 543:1 from 489:1 by etching one Si dummy lot. It demonstrates that etching either Si_3N_4 wafers or bare Si wafers increases the selectivity.

A study on maintaining a stable selectivity was carried out in the bath with 13.5% H_2O at 165°C. Figure 6 illustrates the results. Selectivity was monitored between every product lot and Si concentration was analyzed. The feeding and bleeding apparatus was used. The apparatus recovered the Si increase, caused by etching product lots. The figure shows that the selectivity started at 27:1 and went up to 295:1 after three product lots etched, where silicon concentration was 59.9ppm. The selectivity was brought down to 172:1 by the apparatus's feeding a certain amount of fresh H_3PO_4 and then by its bleeding the same amount out of the bath, where the Si was reduced to 46.5ppm. The selectivity went up again after the 4th product lot etched and was brought down again with repeating the feeding and bleeding. The selectivity was maintained around 172:1 with etching continuously more product lots. Without the feeding and bleeding after the 6th lot, the selectivity went up to 1600:1 by etching three more product lots. At the 1600:1, 81.6ppm of dissolved Si was detected and SiO_2 deposition was detected at a few points on the wafers. The feeding and bleeding made the bath more like a continuous bath than a batch bath. The selectivity recoveries shown in figure 6 demonstrate that a stable selectivity can be maintained for an extended bath life.

Equation 1 describes the mechanism of Si_3N_4 etching, where Si_3N_4 etching is driven by chemical complexation with H_3PO_4. Equation 2 describes the mechanism of SiO_2 etching, where SiO_2 etching is driven by SiO_2's reduction potential (-0.86 volts). H_2SO_4 has a higher reduction potential (0.158 volts) than the SiO_2. When mixing H_2SO_4 with the H_3PO_4, the H_2SO_4 suppresses SiO_2 etching, but has little impact on the Si_3N_4 etching due to the different etching mechanisms. This is why the addition of H_2SO_4 to H_3PO_4 significantly reduced the SiO_2 rate and had little change on the Si_3N_4 rate [5].

Figure 7 shows production data.   These tests were conducted in a production environment, where one product lot was equivalent to 2200 Å Si_3N_4 removal on both sides of 50 wafers. That means that the accumulated 220K Å Si_3N_4 etched equals to one product lot etched, shown in figure 7. A certain amount of H_2SO_4 was added in H_3PO_4 at the beginning of the bath life. Both apparatuses of the DI water spiking and the feeding and bleeding were applied. Figure 7 shows that Si_3N_4 and SiO_2 etching rates were started with 49.2Å/minute and 0.07Å/minute, respectively, and the rates were maintained at

50.6Å/minute and zero in average, gone through 8 product lots and beyond in the production.

Conclusion

Maintaining stable selectivity is a challenge in Si_3N_4 etching with hot H_3PO_4. Our experiments indicated the need to control water content, reduce Si concentration and condition the initial H_3PO_4 chemical in the bath, in order to achieve stable selectivity for a long production. A DI water spiking apparatus with a NIR spectrometer helped to control water content. The feeding and bleeding apparatus reduced Si concentration in the bath. The addition of H_2SO_4 in H_3PO_4 saved the bath's initial conditioning. With all of the implemented changes, stable Si_3N_4 and SiO_2 etching rates were achieved. Both experimental and production tests demonstrated that Akrion's GAMA batch tool is able to start with a high selectivity and maintain stable selectivity for a long period of Si_3N_4 etching production.

References

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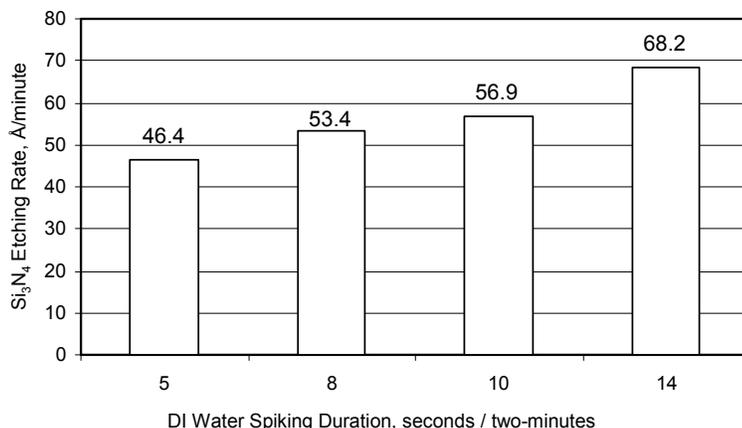
Figure 1. Si_3N_4 etching rate with DI water spikes in H_3PO_4 bath at 165^oC.
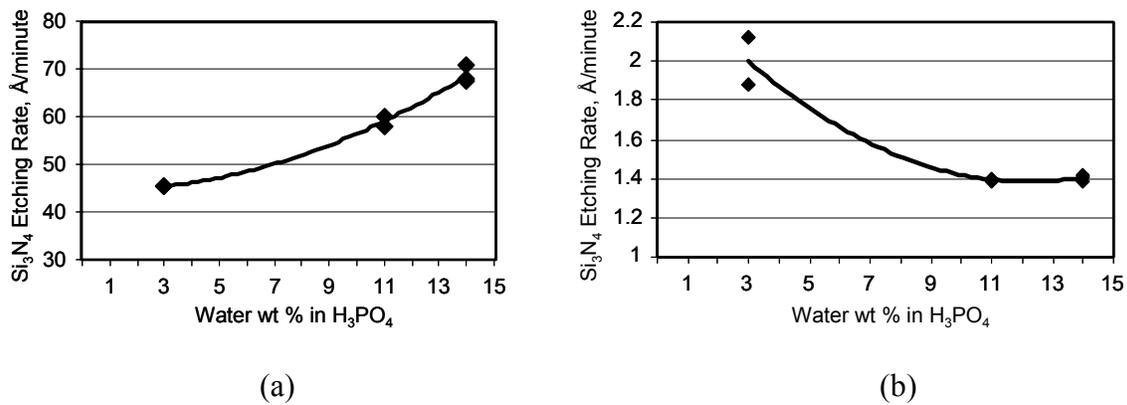
(a)

(b)

Figure 2. Si_3N_4 (a) and SiO_2 (b) etching rates with the change of water concentration in the bath. Both were etched with fresh H_3PO_4 chemical at 165°C.
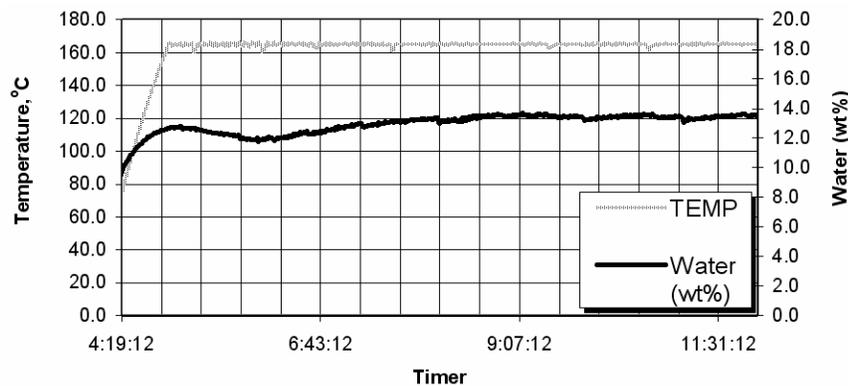

Figure 3. NIR spectrometer's water monitoring in H_3PO_4 bath.
The water concentration is increased at the beginning and stabilized at 13.5% and 165°C, with a routine DI water spike.
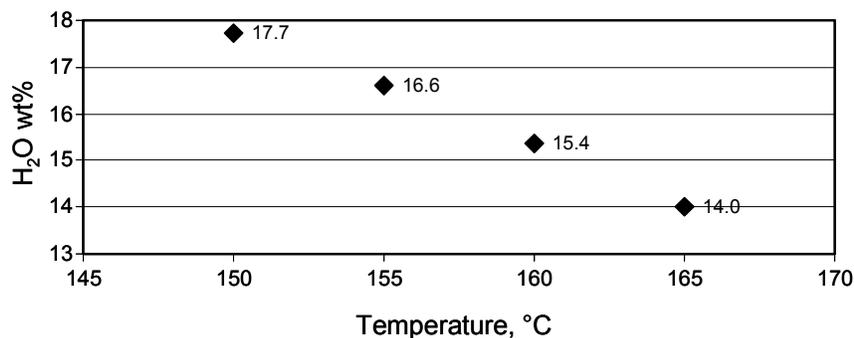

Figure 4. Stabilized water concentrations in the bath at various temperatures with 14seconds/2-minutes of DI water spiking at 165°C.
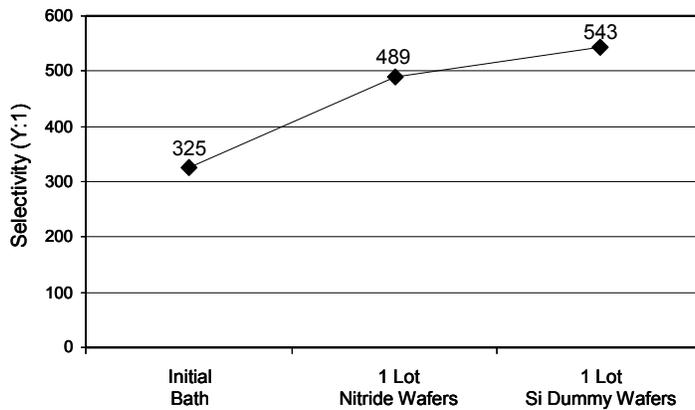
Figure 5. Selectivity increase by etching one lot of Si_3N_4 wafers (50 wafers) followed by etching one lot of Si dummy wafers at 165^oC.
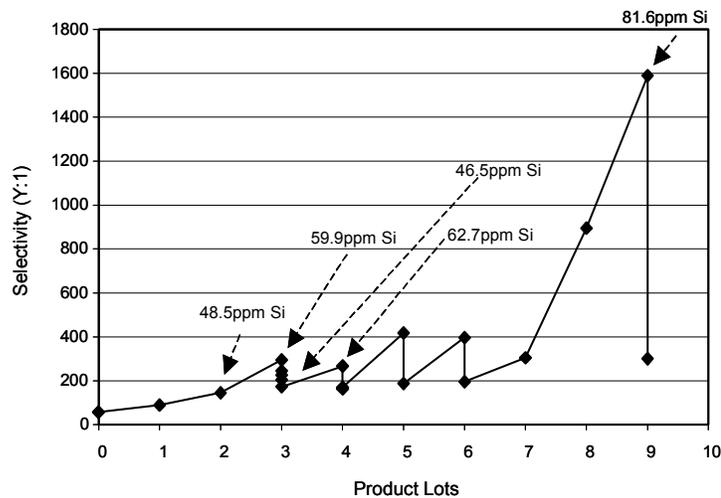

Figure 6. The selectivity increases with etching Si_3N_4 product lots and its recoveries with the chemical feeding and bleeding. A stable selectivity is maintained at $172(Si_3N_4):1(SiO_2)$. Si concentration is increased by 14ppm in average by one product lot etched.
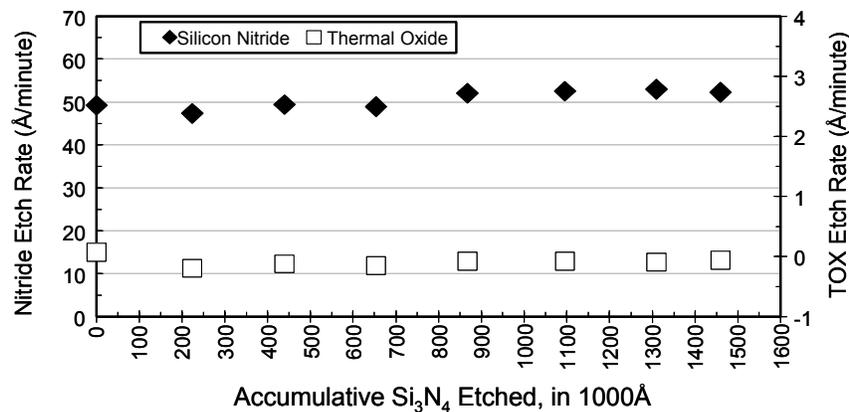

Figure 7. Stabilized Si_3N_4 and SiO_2 (TOX) etching rates. The etching rates are maintained for a long production with the initial addition of H_2SO_4 in H_3PO_4 bath and with the operations of a feeding and bleeding apparatus and a DI water spiking apparatus.