SEMICONDUCTORS

CORRELATION OF BORON BREAKTHROUGH VERSUS RESISTIVITY AND DISSOLVED SILICA IN RO/DI SYSTEM

Historically, dissolved silica has been used to monitor ion-exchange resin in reverse osmosis/deionized (RO/DI) water systems. It is common knowledge that dissolved silica is the first ion that breaks through when the ion-exchange resin is approaching depletion. Recently, the authors correlated boron breakthrough with dissolved silica and associated resistivity drop at Advanced Micro Devices (AMD), Sunnyvale, Calif. As much as 30 parts per billion (ppb) of boron was observed when the dissolved silica was less than 1 ppb. This phenomenon is more dramatic in RO/DI systems that use thin-film composite (tfc) RO membranes.

Introduction

In the production of high-purity water, dissolved silica is one of the most critical parameters used (in addition to resistivity measurement) to monitor ion-exchange resin. Other than the fact that silica can be detrimental to devices (1), it is also known to be the first ion to break through when the ion-exchange resin approaches depletion (2). Much work has been done during the past decade in the areas of removing and measuring silica. One of the improvements made in reducing silica was the switch from cellulose acetate (CA) to tfc RO membranes (3). The tfc membrane has been shown to increase the efficiency of the RO desalination process, especially for the weakly charged ions such as silica. The plant discussed in this article was steadily operated with less than 1 ppb of silica with water of a resistivity of 18+ megohm, and has been low in all other monitored contaminants prior to the switch to tfc membranes about 1 $^1/_2$ *years ago.*

However, an incident occurred in the regeneration immediately following the change of the RO membranes. The resistivity dropped to 17.4 megohm, but the dissolved silica was only 0.6 ppb and the sodium level was 0.01 ppb.

The cause was first thought to be the intrusion of organic compounds such as the trihalomethanes (4), but a series of detailed tests of the water revealed that the resistivity drop was caused by as much as 30 ppb of boron in the water as measured by inductively coupled plasma / mass spectrometry (ICP/MS).

This incident prompted the study of boron breakthrough in AMD-Sunnyvale's RO/DI system. The results of this study showed that boron breaks through much faster than does silica. While the rejection rate of silica improved to 99.92% from 95.35% with the tfc membrane, the boron rejection rate was improved from 31.5% to 59.3%.

Operating Conditions

The RO/DI water system involved is located at AMD-Sunnyvale's Submicron Development Center (SDC) facility. The system consists mainly of two double-pass RO units, primary mixed-bed ion exchange, and polisher beds. This facility monitors the dissolved-silica level continuously using an on-line instrument from Hach Co.; anions and cations using Dionex on-line IC model 8200; and resistivity using a Thornton 770C resistivity meter. The dissolved-silica level has always been less than 1 ppb, sodium less than 0.01 ppb, and the resistivity at 18+ megohm.

Experimental

Boron breakthrough study. One of the primary mixed-bed resin vessels was freshly regenerated. The inlet and outlet water of this vessel was monitored online for resistivity and dissolved silica, and grab samples were taken for boron analysis. The silica was also verified with grab samples. Water samples at the outlet of the mixed-bed resin were collected for boron analysis at gallonage intervals to establish the breakthrough curve. The flowrate was set at

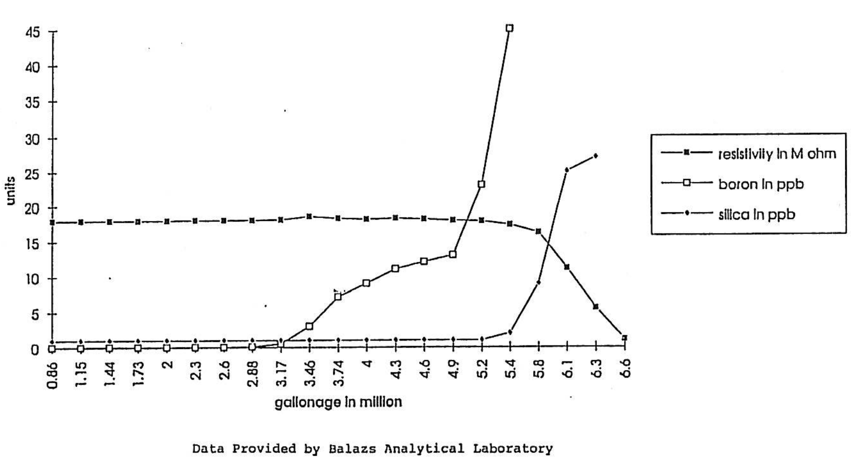

Figure 1. Correlation of boron, resistivity, and silica.

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the normal operating condition of 200 gallons per minute (gpm). The incoming city water and the inlets and outlets of both the CA and tfc membrane were tested for dissolved silica, boron, and the major cations for comparison of the relative rejection rate.

Analytical method of the boron analysis. A lot of work has been done in the analysis of silica, but little has been done in the determination of boron in high-purity water in the semiconductor industry. Up until the last few years, the determination of boron at less than 1 ppb was limited by analytical techniques and equipment.

The ICP/MS approach was used in the determination of boron. This analytical method was validated for the following: a) stability of boron in the bottle, b) reproducibility, c) linearity, d) detection limit, and e) spike recovery.

a) The stability of the boron in the water sample was done by analyzing the same sample a total of 5 times during an 8-day period. Each analysis was either 1 or 2 days apart.

b) The reproducibility test was done by analyzing seven bottles of water samples collected at the same time.

c) The linearity curve was determined using 10-, 20-, 40-, and 200-ppb solutions prepared from a National Institute of Standards and Technology (NIST) boron standard.

d) The detection limit was calculated based on 3 times the standard deviation of the seven replicate samples (b, above).

e) The spike recovery was determined by spiking a water sample with 0.5-, 1.0-, and 2.0-ppb boron standards.

Results and Discussion

Boron breakthrough study. According to the results, boron concentration stayed at less than 0.05 ppb up to about 3 million gallons (for this particular system). It started to break through at around 4 million gallons with boron concentration of up to approximately 0.5 ppb. Boron had a very sharp breakthrough curve, as indicated by Figure 1. The boron concentration went over 10 ppb, while the dissolved silica was still less than 1 ppb. Figure 1 again shows that resistivity cannot be used alone, because as much as 5 ppb of boron had broken through when the resistivity was

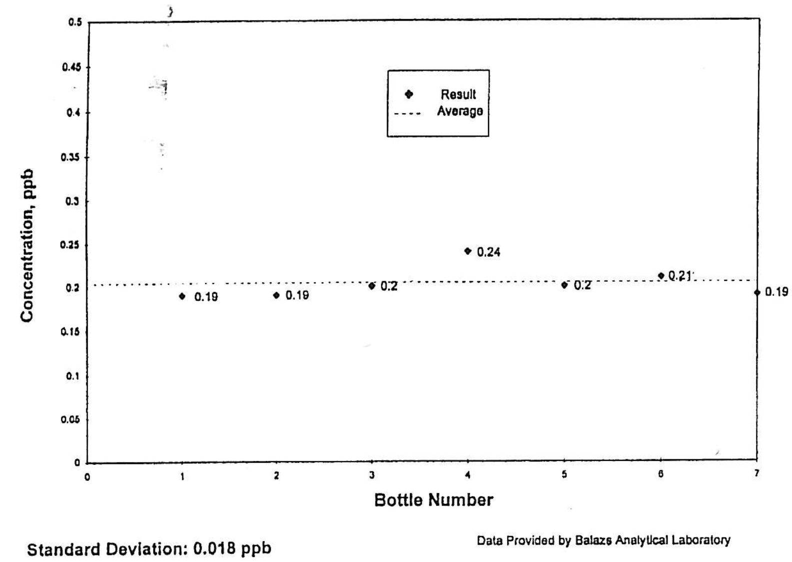

Figure 2. Reproducibility study of boron measurement.

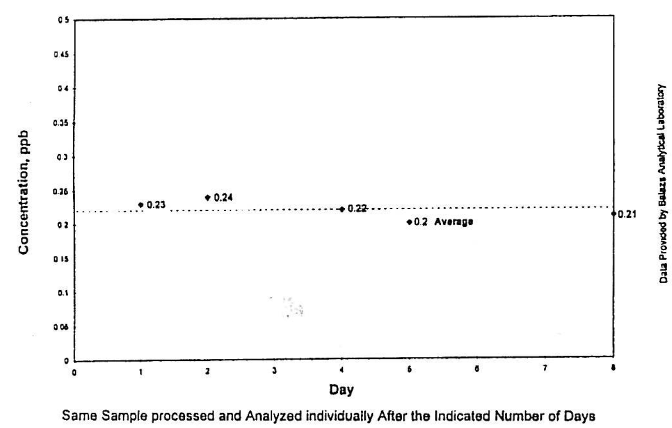

Figure 3. Stability study of boron in high-purity water.

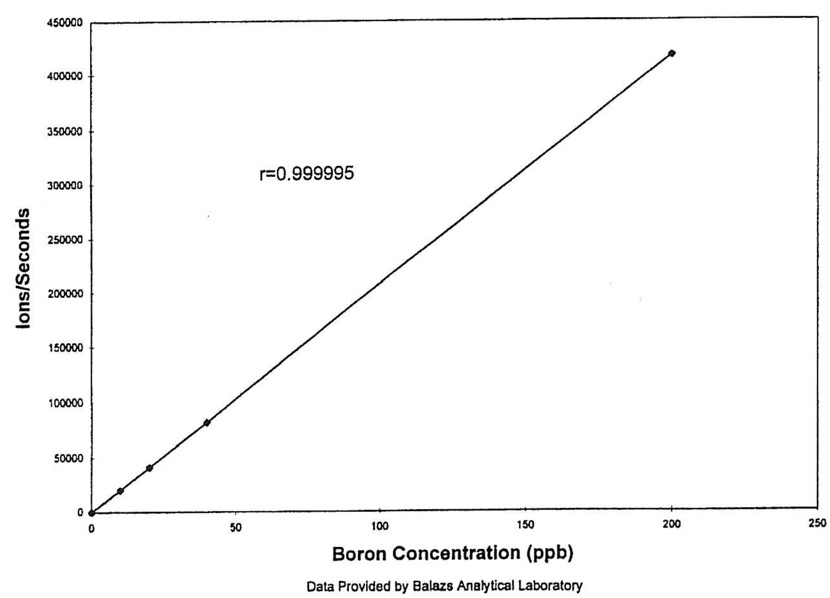

Figure 4. Linear regression for boron.

TABLE A
Comparison of Rejection Rates of CA and tfc Membranes for Silica and Boron

Sample Site	*Silica*	*% Rejection*	*Boron*	*% Rejection*
City water	8,800 ppb	~	130 ppb	~
CA membrane	410 ppb	95.35%	89 ppb	31.50%
tfc membrane	7 ppb	99.92%	53 ppb	59.30%

TABLE B
Percent Spike Recovery of Boron

Concentration Spiked	*% Recovery*
0.5 ppb	95-106
1.0 ppb	100-119
2.0 ppb	120
50 ppb	103

still registered at 18.1 megohm.

The reason that this boron breakthrough phenomenon became more dramatic can be explained via Table A. While the CA membrane was in operation, 410 ppb of silica was being passed to the primary mixed bed, but with only 89 ppb of boron. Boron breakthrough was probably occurring almost simultaneously with the silica. Although testing for boron was not done, the breakthrough probably would not have been noticed because of the much higher concentration of silica. Upon the conversion to the tfc membrane, the silica challenge to the resin dropped to 7 ppb, but boron remained relatively high at 53 ppb. Even though the relative rejection rate for boron improved to a much greater degree, silica feeding into the mixed bed was significantly higher. Therefore, boron breakthrough became the ion that needed to be used to determine the performance of the mixed-bed ion exchange.

Analytical method of boron analysis. The results of the stability, reproducibility, linearity, detection limit, and spike recovery tests are presented in Figures 2, 3, and 4 and Table B, respectively. As shown in Figure 2, boron in high-purity water is stable at least 8 days after sample collection. The analytical method for measuring such low-level boron in high-purity water is proven to be accurate and reliable according to Figure 3. The standard deviation of the samples collected in seven bottles is 0.018 ppb. The detection limit is established at 0.05 ppb, based on 3 times the standard deviation of the seven replicate analyses. The spike recovery is between 90% and 110% (see Table B). The calibration curve is linear from 0 to 200 ppb (Figure 4).

Conclusion

In the operation of AMD-Sunnyvale's RO/DI system, boron is used in addition to silica and resistivity to monitor ion-exchange resin. This is important because one of the dopants used in wafer fabrication is boron. It is known to affect P-N junctions (5). How much boron in high-purity water is tolerable before it is detrimental to the wafer is beyond the scope of this article. The technique of ICP/MS is an accurate and reliable method in the analysis of boron down to 0.05 ppb. The tfc RO membrane is better in reducing silica and other contaminants, and thus reducing operation cost, but one must pay attention to the boron concentration.

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References

1. Pate, K. "Control of Dissolved Silica in High-Purity Water Systems", *ULTRAPURE WATER 9(4)* pp. 35-43 (1992).
2. Hoffman, B.; Gavaghan, M. "A Chemical Approach to Understanding Ion Exchange Performance in Ultrapure Water Systems", *Proceedings of the Semiconductor Pure Water Conference*, pp. 3-21, San Francisco, Calif. (Jan. 10-11, 1985).
3. Walker, D. "A Comparison of Thin-Film Composite (TFC) and Cellulose Acetate Blend Membrane in Ultrapure Water Production", *Proceedings of the Semiconductor Pure Water and Chemicals Conference*, pp. 119-129, San Francisco, Calif. (Jan. 10-11, 1985).
4. Chu, T. "Trihalomethanes Can Cause RO/DI System Problems", *Proceedings of the Semiconductor Pure Water and Chemicals Conference*, pp. 229-252, Santa Clara, Calif. (Jan. 18-20, 1989).
5. Yagi, Y.; Hayashi, F.; Uchitomi, Y. "Evaluation of Boron Behavior in Ultrapure Water Manufacturing System", *Proceedings of the Semiconductor Pure Water and Chemicals Conference*, pp. 54-62, San Jose, Calif. (March 8-10, 1994).

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