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Development of Dissolved Oxygen Removal System Using Nitrogen Gas Bubbling

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ABSTRACT

It is essentially important to remove the dissolved oxygen (DO) in the ultrapure water for the future ultra-large scale integration (ULSI). We have found the existence of the big driving force for the oxygen diffusion through the material that increases the DO concentration. Based on this finding, we have developed the DO removal system made of a low oxygen permeability material with the nitrogen gas bubbling as a point of use purifier. In this system, the residual DO concentration has reached 0.2 ppb at a gas-liquid ratio of 1.2 m^3/m^3 that is ten times smaller than the previously reported data. Furthermore, the other impurities in the ultrapure water do not increase after this process.

INTRODUCTION

The control of the native oxide growth rate on the Si surface is of great importance in the fabrication of ultra-large scale integration (ULSI). Especially, the native oxide growth has to be controlled severely prior to the gate oxidation and so on [1]. The coexistence of oxygen (O_2) and water is required for the growth of the native oxide in the ultrapure water (UPW) at room temperature [1]. Therefore, it is very important to lower the dissolved oxygen (DO) concentration below ppb level in the UPW used in several processes of the ULSI fabrication.

There are many DO removal methods [2]. The lowest residual DO concentration by these conventional methods is still 2-3 ppb in the UPW. Even if the DO concentration has reached sub-ppb level using conventional methods, other contaminations, for instance, the total organic carbon (TOC) has increased. These methods can not be used for the DO removal system as purifiers, and need the additional contamination removal system in the next step. The nitrogen gas (N_2) bubbling method physically removes DO by replacing the DO by N_2 in the UPW [3]. Because the apparatus of this method is so simple that it is relatively easy to prevent the generation of other contaminations by using the pure N_2. The problem of this conventional method is that the DO removal limit is about 20 ppb. The reason why the DO removal limit is so high has been thought to be due to the low velocity of mass transfer and the insufficient contact between gas and liquid phase. However, it can not be disregarded the possibility that the DO concentration is influenced by the O_2 permeation through the material. So, we have considered the permeation rate of O_2 into UPW, and found out the influence of O_2 permeation through the material when the DO concentration is in ppb level.

The purpose of this work is to establish the DO removal system as a point of use purifier in the ULSI fabrication. For this purpose, we have developed the new N2 bubbling system using a low oxygen permeability material made of PVDF and discussed the performance of this DO removal system in this paper.

EXPERIMENTAL

The schematic diagram of DO removal system using N_2 bubbling is shown in Fig. 1. This system consists of 4 towers made of PVDF with 3.4 m in length and 136 mm inner diameter, and these towers are connected in series with PVDF tubes. The UPW at the flow rate of 1.1 m^3/hr enters the top of the first tower and goes down to the bottom, then flows up to the top of the next tower through the connecting tube. The flow rate of N_2 is controlled by a mass flow controller and N2 is supplied from the bottom of each tower through the porous gas sparser. The DO concentration in the UPW was measured at the outlet of each towers by MOCA3600® (made by Orbisphere) whose detection limit was in the order of 0.1 ppb, and the resistivity and TOC concentration were measured at the outlet of this system, as well.

RESULTS & DISCUSSION

Figure 2 shows the relationship between the gas-liquid ratio and the residual DO concentration at different numbers of PVDF towers. The horizontal axis represents the ratio of the N_2 to UPW at each towers. The residual DO concentration decreased with the increase of the gas-liquid ratio at each towers. The DO concentration of the outlet of this system was below 1 ppb at a gas-liquid ratio of 0.5 m^3/m^3 over, and reached 0.2 ppb at a ratio of 1.2 m^3/m^3. This value is ten times smaller than the previously reported data [2]. This result shows that the sub-ppb DO level UPW can be obtained easily only by the N2 bubbling system made of PVDF. Moreover, this result suggests that the big driving force for the O_2 pass through the material exists at ppb level DO concentration, and the equilibrium between the DO removal rate and the O2 permeation rate determines the DO removal limit. Thus, it is very important to choose the low oxygen permeability material for reducing the DO in the UPW.

Figure 3 demonstrates the resistivity and the TOC concentration as a function of the gas-liquid ratio. In the case of varying the gas- liquid ratio, no dependence is shown between the resistivity of 18.0 MΩ•cm and the gas-liquid ratio. The TOC concentration decreases with the increase of the gas-liquid ratio. The occurrence of decreasing the TOC concentration has not been clarified yet. However, the TOC concentration does not increase in the UPW treated by this system. This suggests that this N2 bubbling system can be used for the DO removal system as a point of use purifier.

CONCLUSION

We have found that it is important to choose the low oxygen permeability material for obtaining the UPW at the DO concentration of sub-ppb level. Based on this finding, we have developed the DO removal system made of PVDF using N2 bubbling. In this system, the residual DO concentration decreased with the increase of the gas-liquid ratio, and reached 0.2 ppb at a gas-liquid ratio of 1.2 m^3/m^3 at each towers. This is about ten times smaller than the previously reported data. The TOC concentration in the UPW does not increase after this treatment. This suggests that this system can be used for the DO removal system as a point of use purifier.

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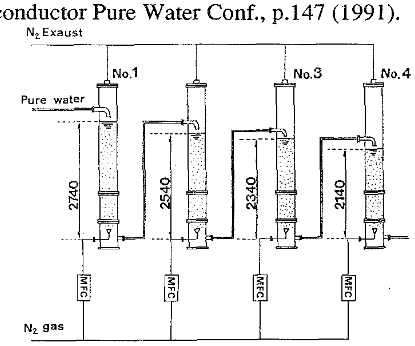

Fig. 1 Schematic diagram of DO removal system using N_2 bubbling.

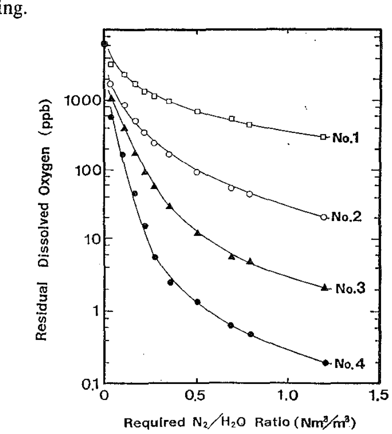

Fig. 2 Relationship between the gas-liquid ratio and DO concentration at different numbers of PVDF towers.

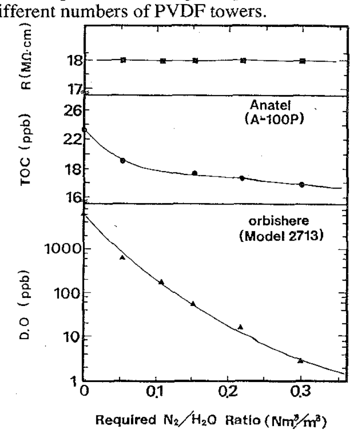

Fig. 3 The resistivity and the TOC concentration as a function of the gas-liquid ratio.