DYNAMIC STRUCTURE OF WATER IN ULTRA PURE WATER PRODUCING SYSTEM OBSERVED BY DIELECTRIC AND ^{17}O -NMR RELAXATIONS

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Key Words: Physical Property, Ultra Pure Water, Dynamic Structure, ^{17}O -NMR, Dielectric Relaxation

In order to observe the influences on microscopic behavior of water molecules caused by water treatment processes, the changes of dynamic structure of water in an ultra pure water (UPW) producing system have been studied by dielectric and ^{17}O -NMR relaxations. The UPW system used in this study consists of typical unit processes employed in current commercial systems for semiconductor manufacturing plants, and produces UPW of the highest quality with specific resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$. Throughout the whole system from city water till UPW dielectric relaxation time, τ_d , is kept constant at about 8.7 ps, while β , a parameter describing the distribution of τ_d , increases with each treatment step, reaching a constant value of about 1.00 after the removal of major impurities by a reverse osmosis membrane. The spin-lattice relaxation time, T_1 , obtained from ^{17}O -NMR is unchanged at about 7.3 ms through all processes in the system. Spin-spin relaxation time, T_2 , shows drastic changes with each treatment step. The changes of T_2 are well explained by proton-exchange reactions in water and should not be related directly with rotational motions of water molecules. These results indicate that the averaged rotational motion of water molecules is unchanged from city water to UPW. The distribution around the average, however, becomes narrower during purification, and the rotational motions of water molecules are highly homogenized in UPW.

Introduction

In semiconductor manufacturing ultra pure water (UPW) is primarily used as a rinsing medium after wet chemical processes. The silicon wafer surfaces fabricated for today's highly integrated and complex circuits allow no contaminants to remain after rinsing. In order to realize this extremely high level of cleanliness, UPW has reached the ultimate purity, approaching that of theoretically pure water, as shown in Table 1 (Ohmi, 1993).

Recently not only purity, but improved cleaning ability is sought after in UPW or dilute aqueous solutions. Due to escalating requirements for environmental protection and demands to lower manufacturing costs, reduction in chemical consumption in wet processes has become an important issue. At the same time, more efficient cleaning media are also required for the continuously rising levels of wafer surface cleanliness. Under these circumstances, water is expected to play an extended role in wet cleaning. Firstly, as a rinsing medium, it

is desirable for UPW to penetrate more rapidly into highly integrated, $0.1 - 1.0 \mu\text{m}$ patterns and wash out completely the chemicals remaining in the pattern after chemical cleaning processes. Secondly, as an alternative to chemicals, the ability of UPW to remove contaminants sticking to the solid surface is desired.

Table 1 An example of guaranteed quality of UPW used in a semiconductor manufacturing plant (Ohmi, 1993)

Item		Guaranteed value
Resistivity	$[\text{M}\Omega \cdot \text{cm}]$	>18.1
Particle	$[\text{ml}^{-1}]$	
$>0.05 \mu\text{m}$		< 5
$>0.1 \mu\text{m}$		< 1
Bacterium	$[\text{ml}^{-1}]$	< 1
TOC ^{a)}	$[\mu\text{g/l}]$	< 2
DO ^{b)}	$[\mu\text{g/l}]$	< 50
SiO_2	$[\mu\text{g/l}]$	< 0.5
Na	$[\mu\text{g/l}]$	< 0.01
Ca	$[\mu\text{g/l}]$	< 0.01
Fe	$[\mu\text{g/l}]$	< 0.01
Al	$[\mu\text{g/l}]$	< 0.01
Cl	$[\mu\text{g/l}]$	< 0.05
SO_4	$[\mu\text{g/l}]$	< 0.1

a) Total organic carbon b) Dissolved oxygen

* Received on September 5, 1995

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** deceased on March 29, 1996

Not only in semiconductor manufacturing, but in the various fields where inorganic and organic chemicals, including halogenated hydrocarbons, are used in cleaning, water with improved cleaning ability will be quite useful. The ideal wet cleaning process should be accomplished by water and dilute innocuous aqueous solutions in the future.

For the improvement in the cleaning abilities of water and dilute solutions, the properties of water such as surface tension, viscosity and solubility should be controlled according to the purpose and role of water in the process. These macroscopic properties are determined by the microscopic behavior of the water molecules. Understanding the microscopic behavior of the molecules is essential to understand the macroscopic phenomena, and to build up the water property controlling technologies.

So far, raising the purity of UPW has been pursued enthusiastically. In these improvements, the characteristics of the water have been described by the amount of impurities, and the performance of each constituent purification process has been evaluated by its impurity reduction efficiency. Very little attention, however, has been paid to the microscopic properties of water molecules in water treatment systems.

In this study we have observed the microscopic behavior of water molecules in a UPW production system by dielectric and ^{17}O -NMR relaxation measurements, as a beginning of the investigations on the relations between microscopic behavior of water molecules and water treatment techniques, for preparation of the development of water property control technology which may extend the role of water in future wet processes.

Fig. 1 Block flow diagram of UPW system used in this study. CF, carbon filter; MF, membrane filter; UVST, ultraviolet sterilizer; RO, reverse osmosis membrane; DAM, membrane degasifier; MBP, mixed bed ion exchanger; UVox, ultraviolet oxidizer; CP, cartridge polisher (small-sized mixed bed ion exchanger); UF, ultrafilter

1. Experiment

1.1 Ultra pure water producing system (UPW system)

A block flow diagram of the UPW system used in this study is shown in **Fig. 1**. The system is a downsized experimental apparatus consisting of all the typical unit processes generally employed in current commercial UPW systems for the semiconductor industry. The qualities of water in the system, shown in **Table 2**, show that the system has been operated normally and has produced UPW of the highest quality accepted in the current semiconductor industry. The system was installed beside NMR and time domain reflectometry (TDR) measuring apparatus to minimize quality loss and property changes of the sample water, especially of UPW,

Table 2 Qualities of water in UPW system

Item		Raw water	Primary pure water	UPW
Conductivity	[$\mu\text{S}/\text{cm}$]	126	1.75	—
Resistivity	[$\text{M}\Omega\cdot\text{cm}$]	—	0.58	18.2
Particle	[ml^{-1}]	—	—	—
>0.05 μm		—	—	4
>0.1 μm		—	—	0
Bacterium	[ml^{-1}]	—	—	0.1
TOC ^{a)}	[$\mu\text{g}/\text{l}$]	730	70	1.0
DO ^{b)}	[$\mu\text{g}/\text{l}$]	8.96×10^3	8.83×10^3	9.1
SiO ₂	[$\mu\text{g}/\text{l}$]	22.3×10^3	0.34×10^3	0.04
Na	[$\mu\text{g}/\text{l}$]	40.0×10^3	0.25×10^3	<0.003
Ca	[$\mu\text{g}/\text{l}$]	16.2×10^3	<0.5	<0.003
Fe	[$\mu\text{g}/\text{l}$]	< 0.03×10^3	<1.0	<0.005
Al	[$\mu\text{g}/\text{l}$]	< 0.01×10^3	<1.0	<0.005
Cl	[$\mu\text{g}/\text{l}$]	4.2×10^3	13	<0.05
SO ₄	[$\mu\text{g}/\text{l}$]	2.5×10^3	1.0	<0.1

a) Total organic carbon b) Dissolved oxygen

which is subject to being contaminated due to contact with air, among other factors.

1.2 Dielectric relaxation measurements

Dielectric relaxation measurements were carried out with a digitizing oscilloscope (Yokogawa Hewlett Packard HP-54121) utilizing TDR (Cole, 1975a, 1975b, 1980, Umehara *et al.*, 1990). The measurement system was set to cover a frequency range from 100 MHz to 20 GHz. The step pulse rise time and voltage increase were 35 ps and 200 mV, respectively. On-line measurements were made in all TDR measurements; *i.e.* outlet water from each process in the UPW system was fed to the TDR detection cell directly and measured while it flowed through the cell. The temperature of the sample water was controlled to be $25.0 \pm 0.1^\circ\text{C}$ by a heat exchanger positioned before the TDR cell. 128 reflected pulses were integrated in each measurement, and the measurements were repeated ten times for each sample.

1.3 ^{17}O -NMR relaxation measurements

The ^{17}O spin-lattice relaxation time, T_1 , and full width at half amplitude of Lorentzian, Hw , were measured with a FT NMR spectrometer (JEOL EX-400). T_1 was measured by the ordinary inversion recovery method with a pulse sequence of $180^\circ - t - 90^\circ$ pulses. The T_1 value for each water sample was determined from a series of measurements with 16 different time intervals, t , and a waiting time which was greater than ten times of T_1 . The spin-spin relaxation times, T_2 , presented in this article are derived from linewidth measurements. The NMR absorption signal of ^{17}O is described by a Lorentzian function, and its full width at half amplitude, Hw , is connected with T_2 by $T_2 = 1/(\pi Hw)$. The free induction decay signals were integrated 160 and 3200 times in T_1 and Hw measurements, respectively. Quartz tubes of 5 mm diameter were used in the measurements. Sample water from each process of the UPW system was drawn into the quartz tube after passing through a heat exchanger adjusting the temperature to $25.0 \pm 0.1^\circ\text{C}$, and overflowed to in a water bath where temperature was controlled to be in the same range. After sampling, T_1 and Hw were measured immediately while keeping the temperature of the sample water within $25.0 \pm 0.2^\circ\text{C}$. T_1 and Hw were reproducible to within 2%.

2. Results and Discussion

2.1 Dielectric relaxation time and its distribution

The dielectric relaxation of water is described by the Cole-Cole representation:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (i\omega\tau_d)^\beta]} \quad (1)$$

where ε^* and ε_∞ are the complex permittivity at

Fig. 2 τ_d and β of water in UPW system. 1, city water; 2, carbon filter; 3, membrane filter; 4, ultra violet sterilizer; 5, reverse osmosis membrane; 7, primary pure water; 8, membrane degasifier; 9, mixed bed ion exchanger; 10, ultraviolet oxidizer; 11, cartridge polisher; 12, UPW

angular frequency ω and the permittivity extrapolated to $\omega = \infty$, respectively. $\Delta\varepsilon$ is the relaxation strength, τ_d is the dielectric relaxation time, and β is a parameter describing the distribution of relaxation times. The frequency dependence of ε^* is directly measured by the TDR method. A typical ε^* of water as a function of ω is shown in reference (Kaatze, 1989). τ_d and β were obtained from Eq. (1) using a least-squares fitting procedure. In the fitting procedure, ε_∞ was fixed at 5.2, and $\Delta\varepsilon$ was allowed to vary slightly from 73.0. These are generally accepted values for both the parameters (Kaatze, 1989). τ_d and β values for water passing through the UPW system are shown in Fig. 2. Through all the processes of the UPW system, τ_d remains constant at around 8.7 ps. τ_d detected for UPW was 8.71 ps at 25°C . τ_d indicates the averaged rotational movability of water molecules in the sample. The constancy of τ_d shows that the averaged rotational motion of water molecules does not change from city water to UPW. On the other hand, β increases with each treatment step, and reaches a constant close to 1.000 after being treated by a reverse osmosis (RO) membrane. This change of β indicates that the distribution of the rotational motions of water molecules narrows with proceeding treatment steps, and is highly homogenized after RO treatment.

As shown in Table 2, raw water includes various kinds of impurities, including ions, organic materials, and dissolved oxygen in the order of mg/l. These impurities cause many different kinds of interactions with water molecules according to their size, charge, hydrophobicity, and other properties, and result in various rotational movabilities of water molecules in the raw water. After major impurities are removed by RO, only $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions dominate, with very few other kinds of interactions made by residual

impurities. The change of β observed in Fig. 2 can be explained by this change of homogeneity in interactions around water molecules.

This finding implies that β can be used as an index for water purity, which is sensitive to various kinds of impurities by itself, and is not limited to a certain kind or group of impurities. In Fig. 2, the scatter of β seen in the first several steps in the UPW system converge within an error of ± 0.002 after RO treatment. This also reflects the inhomogeneities in the interactions around water molecules before RO, and homogeneities in pure water and UPW. The scatterings in β values in repetitive measurements of TDR will also help the determination of water purity.

2.2 Spin-lattice and spin-spin relaxation rates of ^{17}O -NMR

The ^{17}O nucleus is a quadrupole nucleus with spin quantum number of $5/2$, and its nuclear relaxation is mainly caused by the interaction between the electric quadrupole moment of the ^{17}O -nucleus and the electric field gradients in the molecule. In this case, the relation between the spin-lattice relaxation rate, $R_1 (=1/T_1)$, and the reorientational correlation time, τ_c , is given by

$$R_1 = \frac{3\pi^2}{10} \left(\frac{2I+3}{I^2(2I-1)} \right) \left(\frac{e^2qQ}{h} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \tau_c \quad (2)$$

where I , η , and e^2qQ are the spin, asymmetric parameter, and quadrupole coupling constant, respectively (Abragam, 1961, McConnell, 1987). τ_c of the ^{17}O nuclei furnish information on the reorientational motion of the perpendicular axis to the H_2O molecular plane as shown in Fig. 3. As seen in eq. (2), τ_c is proportional to R_1 . The orientational motions of water molecules can be derived from the measurement of T_1 . On the other hand, the spin-spin relaxation time, T_2 , is effected by both the orientational motions of water molecules and the rate of proton exchange reactions in water (Meiboom, 1961). The difference between T_1 and T_2 represents the contribution of the proton exchange reaction as described later.

Spin-lattice relaxation rate, R_1 , and spin-spin relaxation rate, R_2 , obtained from ^{17}O -NMR measurements are shown in Fig. 4. R_1 remains constant at about 138 sec^{-1} , while R_2 shows a drastic change with each treatment step. By using reference parameters (Shimizu and Taniguchi, 1991), τ_c was calculated to be 1.8 ps. Similarly to τ_d , τ_c represents the averaged rotational movability of water molecules. The constancy of R_1 in Fig. 4 reveals that the averaged rotational motion of water molecules does not change throughout the whole UPW system, which is in good agreement with the result of τ_d .

The drastic change of R_2 can be explained by proton exchange reactions in sample water. Meiboom proposed that pH dependence of R_2 can be

Fig. 3 Reorientational correlation time, τ_c , of H_2O molecule

Fig. 4 R_1 and R_2 of water in UPW system. 1, city water; 2, carbon filter; 3, membrane filter; 4, ultra violet sterilizer; 5, reverse osmosis membrane; 6, RO reject; 7, primary pure water; 8, membrane degasifier; 9, mixed bed ion exchanger; 10, ultra-violet oxidizer; 11, cartridge polisher; 12, UPW

described by the following equations (Meiboom, 1961):

$$R_2 - R_1 = \tau_h \sum_i \frac{P_i \delta_i^2}{1 + \tau_h^2 \delta_i^2} \quad (3)$$

$$\tau_h^{-1} = \frac{2}{3} k_1 [\text{H}^+] + k_2 \frac{K_w}{[\text{H}^+]} \quad (4)$$

where τ_h , P_i , and δ_i are the average time for a proton bonding to a specific oxygen, the relative intensity of the i th line in a triplet of an ^{17}O signal, and the frequency difference between the i th line and dominant line, respectively. K_w is the dissociation constant of water ($1.0 \times 10^{-14} \text{ mol l}^{-1}$ at 25°C). k_1 and k_2 are the proton exchange rate constants:

Fig. 5 pH dependence of $R_2 - R_1$. 1, city water; 2, carbon filter; 3, membrane filter; 4, ultra violet sterilizer; 5, reverse osmosis membrane; 6, RO reject; 7, primary pure water; 8, membrane degasifier; 9, mixed bed ion exchanger; 10, ultraviolet oxidizer; 11, cartridge polisher; 12, UPW; 13, UPW bubbled with CO_2 (pH 4.0); 14, UPW bubbled with CO_2 (pH 4.9). Value calculated by Eqs. (3) and (4) is given by solid line

The $R_2 - R_1$ obtained in the present study is plotted in Fig. 5 with a curve (solid line) calculated by Eqs. (3) and (4). In Fig. 5 the data of UPW bubbled with CO_2 (plots No. 13 and 14) are added so as to have plots in the acidic region and show the large influence of air contamination in T_2 measurements of ^{17}O on UPW. In the calculation, k_1 and k_2 were determined by the least-squares procedure to be 6.56×10^9 and $4.94 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively, which is consistent with the literature (Meiboom, 1961) within experimental error. The calculated curve reproduces experimental results very well. In the UPW system, the pH of water changes by ion removal, and CO_2 production by the decomposition of organic materials as shown in Fig. 5. It is clear that the drastic change of R_2 in the present system is completely explained by proton exchange reactions in the sample water. In addition it is confirmed that the measurement on UPW with the greatest possible care for prohibiting contamination gives a T_2 value in good agreement with the value for water of neutral pH expected by proton exchange mechanism.

Conclusion

Using TDR and ^{17}O -NMR measurements, we have observed the physical properties of water in the UPW producing system. The consistency of τ_d and τ_c through the whole system has shown that the averaged rotational motion of water molecules does not change during any treatment steps in the UPW system from city water to UPW. However, the change of β has

revealed that the distribution of the rotational motions of water molecules becomes narrower with each purification process and is highly homogenized in UPW. β can be used as a novel index for water purity sensitive to various kinds of impurities. τ_d , β , R_1 , and R_2 in UPW at 25°C of the highest quality utilized in the current semiconductor industry were 8.71 ps , 0.999 ± 0.001 , 138 s^{-1} , and 373 s^{-1} , respectively. The drastic change of R_2 in the UPW system was clearly explained by proton exchange mechanism, and should not be directly correlated with the rotational motion of water molecules.

We have started a basic investigation on the relationship between dynamic structure of water and water treatment technology, and observed that the rotational motions of water molecules are highly homogenized in UPW. For shedding light on the hidden functions of water and utilizing them in future industries, it will be more and more important to understand the microscopic behavior of water under various conditions.

Nomenclatures

e^2qQ	= quadrupole coupling constant	[Hz]
Hw	= full width at half amplitude of NMR signal	[Hz]
I	= spin quantum number	[—]
Kw	= dissociation constant of water	[mol l ⁻¹]
k_1	= proton exchange rate constants	[l mol ⁻¹ s ⁻¹]
k_2	= proton exchange rate constants	[l mol ⁻¹ s ⁻¹]
P_i	= relative intensity of i th line in a triplet of ^{17}O -NMR signal	[—]
R_1	= spin-lattice relaxation rate ($=1/T_1$)	[s ⁻¹]
R_2	= spin-spin relaxation rate ($=1/T_2$)	[s ⁻¹]
T_1	= spin-lattice relaxation time	[s]
T_2	= spin-spin relaxation time	[s]
β	= parameter describing distribution of dielectric relaxation times	[—]
δ_i	= frequency difference between the i th line and dominant line in triplet of ^{17}O -NMR signal	[rad·s ⁻¹]
$\Delta\epsilon$	= dielectric relaxation strength	[—]
ϵ_∞	= permittivity extrapolated to $\omega=\infty$	[—]
ϵ^*	= complex permittivity	[—]
η	= asymmetric parameter	[—]
τ_c	= reorientational correlation time	[s]
τ_d	= dielectric relaxation time	[s]
τ_h	= average time for proton to be bonded to oxygen	[s]
ω	= angular frequency	[Hz]

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