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Contribution of the contamination of deionized water by bacteria to the adsorption of carbon on Si and GaSb

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Auger electron spectroscopy analysis was performed on GaSb and Si semiconductor surfaces rinsed by deionized water or by tap water. The surface contaminations deduced from these analyses were correlated to the results of chemical and bacteriological tests of deionized tap water and it was found that the development of micro-organisms in the water-line was responsible for a carbon contamination of the samples rinsed by deionized water.

1. Introduction

Ultra-pure water is used extensively in the manufacture of semiconducter devices, either by itself or as a solvent for other compounds, in cleaning surfaces or in etching samples. Several methods have been proposed to obtain ultrapure water: ion-exchange resin, distilling systems, reverse osmosis process, etc. Often several complementary methods for purifying water are used in order to obtain the best results.

Usually the efficiency of the treatment is monitored by physical parameters (pH, resistivity) or by chemical analysis. However, water-treatment systems can also serve as a medium for the development of bacteria, which these measurements cannot detect. These micro-organisms can utilize a broad range of compounds and sources of energy, and may survive and multiply under the most severe conditions. Thus they are frequently present in ultra-pure water regardless of the purifying system employed [1–5].

A critical step for the growth of high-quality films by molecular beam epitaxy (MBE) is substrate cleaning. Carbon contamination is frequently found on the substrates, and is very difficult to eliminate [6]. As water is often used in substrate preparation, it is necessary to determine the influence of its chemical and bacteriological pollution on the substrate impurities. Thus the surface of GaSb and Si semiconductor samples rinsed by water were studied by Auger electron spectroscopy (AES). The purity level of the water was determined by physico-chemical and bacteriological analysis and was compared with the AES results.

2. Experimental procedure

2.1. Preparation

The experiments were performed on GaSb and Si (0 0 1) oriented surfaces. The samples (1×1 cm^2) were prepared using a standard method prior to MBE. They were then degreased by immersion in hot and cold trichloroethylene, rinsed in methanol, and soldered with In on Mo block holders. Each Mo block received two samples: one of GaSb and one of Si, allowing comparison of the effects of the experimental conditions on two different surfaces. Afterwards the surfaces were polished by a Br_2/methanol solution (1.0 and 0.5%) and rinsed under a water flow for 3 min. The surfaces were then blown dry with N_2 and inserted into a ultra-vacuum chamber (pressure limit 10^{-10} torr) equipped with an Auger electron spectroscopy analyser.

The cleaning described above was done in an horizontal flow bench. The sources of water were:

(A) tap water or deionized water using the system shown in Fig. 1 through one of the possibilities:
(B) one module of activated charcoal (AC1), four modules of ion-exchange resin (IE) and a permanent filter of 0.2 μm (F1);
(C) the same elements as (B) but with another module of activated charcoal, i.e. AC1 was exchanged for AC2;
(D) AC2, 3IE, a module of resin (M) for removal of small particles (> 0.1 μm) and F1;
(E) the same elements as (D) with a sterilized disposable filter of 0.2 μm introduced at the end of the process.

Experiments A–C (first series) were performed some days before D–E (second and third series). The system was not operated between these series.

2.2. Analysis

Just before exposure of the surfaces to the flow, we measured the resistivity and pH and collected a sample of the water in order to perform bacteriological and chemical analyses.

The samples of water were collected under strictly aseptic conditions. The tap of our horizontal flow bench was cleaned and sterilized; flasks of 1 l were

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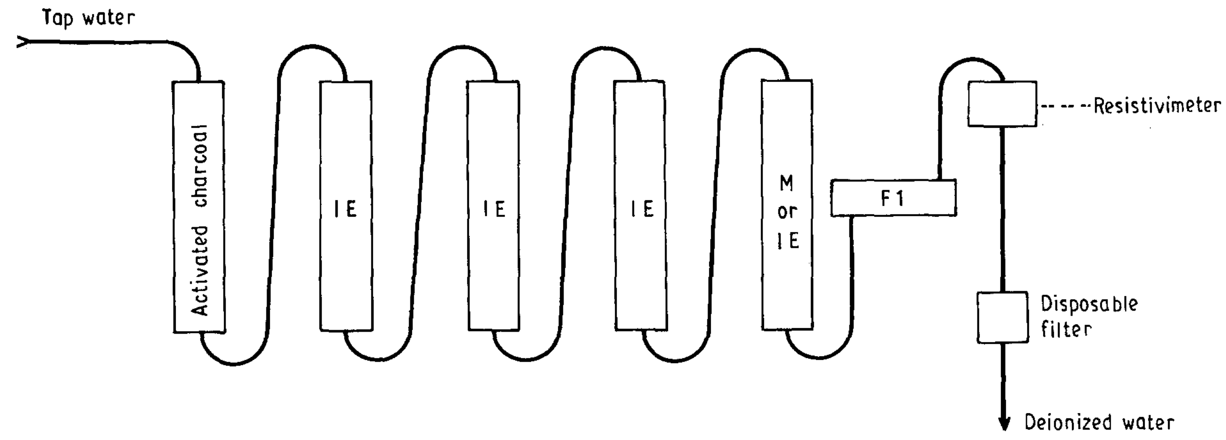

Figure 1 Water-treatment system. IE: ion exchange resin; M: module of resin to remove small particles; Fl: permanent filter of 0.2 μm.

used. After filling them, the flasks were sealed and sent for examination. The chemical analyses were performed with an atomic absorption spectrometer (Varian AA-275). Total bacterial counts were obtained using the spread-plate technique [7] with standard methods agar (Difco). Colonies were counted after 48 h incubation at 37 °C.

The AES spectra of the surfaces were obtained with a cylindrical mirror analyser (CMA) spectrometer. Incident-beam energy of 3 keV and modulation voltages, *E*, of 2 and 4 V were used. In order to evaluate the impurity concentration, we assumed that the Auger emission intensity corresponding to a given element X was proportional to its concentration and sensitivity [8].

TABLE I Chemical analysis of tap water (sample A) and deionized water (sample D).

Parameter	Tap water ($\mathrm{mg\,l^{-1}}$)	Deionized water ($\mathrm{mg\,l^{-1}}$)
Residue after drying at 110 °C	431.0	1.2
Total organic carbon	–	< 1.0
SiO	5.4	0.1
Na^+	17.6	< 0.05
Ca^{2+}	123.0	< 0.05
Cu	< 0.02	< 0.02
Cl^-	34.2	–
HCO^-	323.0	< 6.0
pH	7.28	5.9

3. Results and discussion

The resistivity of the sample of tap water was in the range 1–2 kΩ cm. The resistivity of pure water was allowed to rise up to 18 MΩ cm prior to use, ensuring that the ion density was satisfactorily reduced. This method of control is based on the principle that the conductivity of an electrolyte is the sum of the contribution made by the anions and the cations (The conductivities at 25 °C in $\mu\mathrm{S\,cm^{-1}}$ by $\mathrm{mg\,l^{-1}}$ for HCO (0.75), Na (2.13), Cl (2.14) and Ca (2.60), with the results in Table I, allow us to estimate the resistivities of 1.7 kΩ cm for tap water and at least $M \times \mathrm{cm}$ for deionized water). Thus a weak conductivity (or great resistivity) corresponds to small concentrations of ions. Indeed, as shown in Table I, deionized water presents a high degree of chemical purity, while tap water is particularly rich in bicarbonates and calcium, among other impurities. Traces of Cl, also present in tap water, were absent in deionized water.

The pH values of tap water and deionized water at room temperature were 7.28 and 5.9, respectively. The first value corresponds to hard water, and the second is close to the theoretical calculation $\mathrm{pH} = 1/2\mathrm{pK} - 1/2\log C$, where $\mathrm{pK} = 6.4$ and C (10^{-5} M) is the concentration of dissolved CO, as determined by Henry's law [9].

The total bacteria counts of the samples are shown in Table II. The small quantity of bacteria in tap water can be attributed to the presence of Cl^-. On other hand, the samples of deionized water were very rich in these

TABLE II Series of bacteriological analysis performed with different combinations of the modules described in Fig. 1.

Series	Treatment*	Bacteria count (per 100 ml)	Sample
1	Tap water	23	A
	After AC1 + 4IE + F1	304	B
	After AC2 + 4IE + F1	810	C
	After AC2 + 3IE + M + F1	320	
2	AC2 + 3IE + M + F1:		
	After AC2	23000	
	Before F1	3000	
	After F1	12000	D
3	D + F2	4	E

* AC: Activated charcoal; IE: ion-exchange resin; F1: 0.2-μm permanent filter; M: resin to remove small particles (0.1 μm); F2: disposable filter.

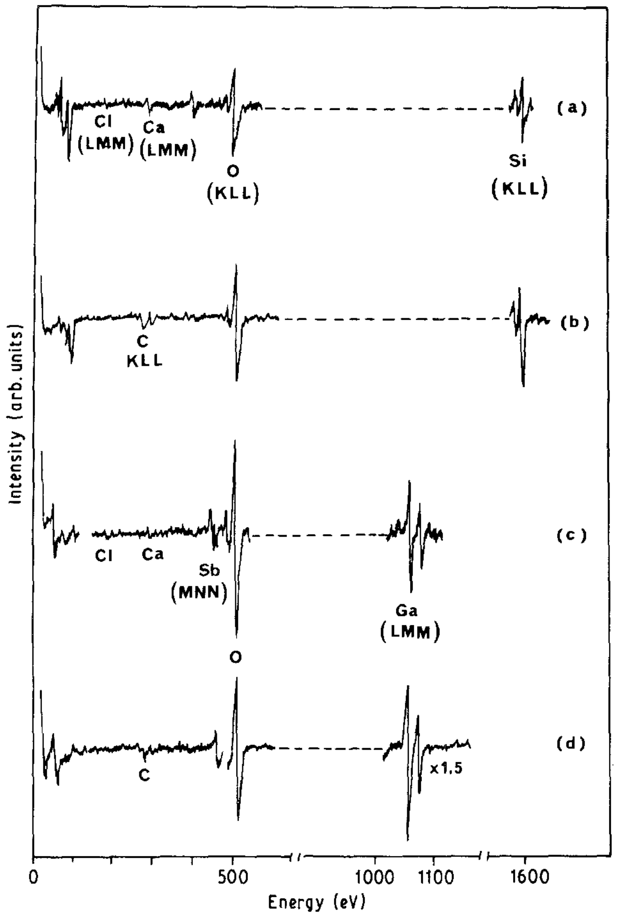

Figure 2 Auger spectra for surfaces of Si; (a) Tap water; (b) deionized water; and GaSb: (c) tap water; (d) deionized water.

micro-organisms. The levels of contamination were dependent on the conditions of the experiment, but in deionized water the levels were always much greater than in tap water. Particularly, between the first and the second series (Table II), when the system was not being operated, the number of colonies in the waterline increased noticeably. Thus in the second series of experiments we tried to find their source. For this purpose the system was cut at three points (after AC, before F1 and after F1) and samples of water were examined from each. Biological contamination was more important after AC and after F1, but between them it was reduced; this result was not surprising, and is easily understood if we take into account that AC and Fl holds back organic materials, which may be used as food by growing micro-organisms.

The Auger spectra of the surfaces are shown in Fig. 2. The surfaces rinsed with tap water (Fig. 2a for Si, 2c for GaSb) were contaminated by oxygen (KLL emission), traces of Cl and Ca (LMM emission) and very small quantities of C (KLL emission). The evaluation of C (Table III) was performed with spectra of increasing sensitivity corresponding to the energy range. On the other hand, the surfaces washed by deionized water (Fig. 2b and d) were free of Cl and Ca, but the amplitude of the peak of C was clearly higher. GaSb surfaces were always richer in impurities than Si surfaces, but the increase in carbon occurred simultaneously on the two surfaces and can be related to the treatment.

The density of bacteria in the samples of water, and the amount of carbon at the surfaces cleaned with these samples were found to increase together. In order to show that the bacteria are responsible for the presence of the carbon, a third series of experiments was carried out. In this series, one set of surfaces was rinsed under the same conditions as D experiment and another set as (E) with a disposable 0.2-μm sterilized filter at the end of the process. This filter was used to eliminate the micro-organisms found by the culture tests. As anticipated, the surfaces prepared in the presence of this filter revealed a noticeably smaller amount of carbon. As the bacteriological analysis detected only four micro-organisms per 100 ml, we conclude that the microflora was largely responsible for the carbon contamination at the surfaces. Nevertheless, the surface with the least amount of carbon remained surface A. It appears that although the last filter retained the micro-organisms and large debris, it could not stop debris smaller than 0.2 μm (from the colonies in the water line) from passing through and coming into contact with the surface.

The total amount of carbon (organic plus inorganic) found in deionized water was always very slight and much lower than in tap water. The total amount of organic carbon in deionized water was also very small, but in a form that can be fixed easily at the surface of

TABLE III Concentration of C and O on GaSb and Si surfaces after treatments (see text) using a sample of water contaminated by different concentrations of microflora.

Sample	AES results GaSb		Si		Bacteria count (per 100 ml)
	C(%)	O(%)	C(%)	O(%)	
A (tap water)	2.0	32	2.0	9.8	23
B (AC1 + 41E + F1)	4.2	28	2.9	8.0	304
C (AC2 + 41E + F1)			3.0	6.6	810
D (AC2 + 31E + M + F1)	4.7	29	4.5	12	12000
E (D + disposable 0.2 -μm filter)	2.5	30	2.6	12	4

semiconductor layers, as may be deduced from our experiments.

4. Conclusion

Semiconductor surfaces rinsed with ultra-pure water can be contaminated by noticeable amounts of carbon, which are demonstrated by bacterial growth in the water-treatment system. Even when the micro-organisms are removed by filters at the end of the water-line, small debris produced by the colonies pass through and come into contact with the samples. In this event, the physicochemical parameters normally used to check the purity levels of the water are not sufficient for this type of application; bacteriological analysis and a reliable removal of micro-organisms must be used.

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