DETERMINATION OF Na CONTENT OF MOS OXIDE LAYERS BY MEANS OF COMBINED SIMS AND BT INVESTIGATIONS

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1. Introduction

It is well known that ionic instability is a very important factor influencing the quality of MOS devices [1]. The quantity and distribution of mobile ions is not easy to determine: the MOS oxides are usually very thin (100 nm and less) and the conventional analytical methods (e.g. neutron activation analysis) combined with a stepwise etching procedure are of too bad depth resolution ($\sim$20 nm), while most modern analytical tools (e.g. Auger electron spectrometry) have too low sensitivity to measure in this concentration range.

SIMS is a convenient method for depth profiling of MOS structures, however, in most cases it does not provide quantitative data [2—4]. A combination of SIMS with activation analysis is fruitful, but not easy to perform [4].

In the present paper a method based upon the combination of SIMS with BT (bias — temperature) test providing a simpler access to quantitative data for the Na content of MOS oxides is presented.

In the second part of the paper the thermodynamic theory of surface accumulation has been adapted for the case of the sodium pile-up at the $Si-SiO_2$ interface.

2. Experimental

The SIMS measurements were carried out by a modified Balzers equipment. For sputtering we used Ar^+ primary ions with 3 keV energy. The ion beam was directed at 60° to the surface normal. The primary ion current density was $1 \cdot 10^{-5}$ Acm^{-2}.

The residual pressure in the vacuum chamber was about $5 \cdot 10^{-7}$ Pa.

The samples were $Si-SiO_2$ structures, with thin ($\sim$20 nm) oxide layers grown in HCl atmosphere at 1100 °C (ambient: $O_2 + N_2 + 4$ vol.% HCl). The oxide thickness was measured by ellipsometry. The contacts were electron-

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-gun evaporated aluminium dots with a diameter (3.2 mm) that was greater than that of the bombarded area (about 2.5 mm). These aluminium dots have been used for BT tests, but were chemically etched off before the SIMS experiments.

First the samples were measured using the high frequency C—V technique [6] at 1 MHz and the flat band voltage (V_{FB}) was determined.

Then the samples originating from the same wafer were parted into two groups. One has been analysed by SIMS without BT test (OBT), the other has been stressed with a positive field of $E_{BT} = 5 \cdot 10^5$ Vcm^{-1} at $T_{BT} = 270$ °C for 15 minutes. A subsequent CV measurement allowed to determine a flat band voltage shift, as high as $\Delta V_{FB} = -2.7$ V.

After the BT test had been accomplished a SIMS analysis of the stressed samples followed, too.

The SIMS measurements reported here were carried out by the reactive SIMS method, i.e. $p \approx 2 \cdot 10^{-4}$ Pa oxygen ambient was present during the measurement. This method is useful, for it provides ion yields relatively intact of so-called matrix effects [7, 8]. The recorded Na^+ profiles are shown in the figure.

3. Interpretation of the results

Our basic assumption is that the flat band voltage in the initial conditions is determined by the fixed charge Q_{fix} and ionic charge q[Na] (where q is the elementary charge and [Na] is the Na surface concentration of Na^+ ions) according to their localization:

$$Q_{fix}\, d_{fix} + q\,[Na]\, d_{Na} = V_{FB}\, \varepsilon_{0x}\, \varepsilon_0\,, \tag{1}$$

where d_{fix} stands for the charge centroid of the fixed charge being unknown, while $d_{Na} = 14.3$ nm is the charge centroid of the sodium ions can be derived from the SIMS profile. ε_{0x} and ε_0 are the dielectric constants of the SiO_2 layer and of the vacuum, respectively.

On the other hand, after the BT test

$$Q_{fix}\, d_{fix} + q\,[Na]_{BT}\, d_{BT} = V_{FB\,BT}\, \varepsilon_{0x}\, \varepsilon_0 \tag{2}$$

where $d_{BT} = 16.3$ nm is the localization of sodium ions after the BT test and

$$V_{FB\,BT} = V_{FB} + \Delta V_{FB} \tag{3}$$

From the difference of equations (1) and (2) we obtain

$$[Na] = \frac{\Delta V_{FB}\, \varepsilon_{0x}\, \varepsilon_0}{q\left(d_{Na} - \frac{[Na]_{BT}}{[Na]}\, d_{BT}\right)} \tag{4}$$

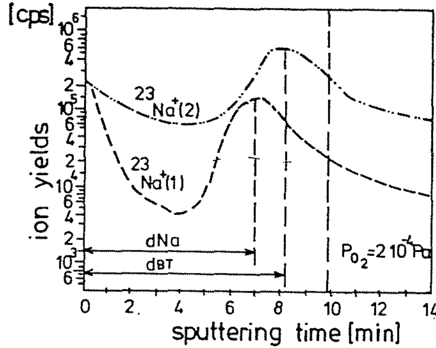


Fig. 1. Na^+ ion yields as measured by reactive SIMS method before and after the bias–temperature (BT) stress

The ratio is

$$\frac{[Na]_{BT}}{[Na]} = 4.5 \tag{5}$$

as it can be determined from the values of the intensity maxima of Na^+ profiles in the transition layer. So we obtain $[Na] = 1.3 \cdot 10^{12}\ cm^{-2}$ and $[Na]_{BT} = 5.9 \cdot 10^{12}\ cm^{-2}$.

The accuracy of these values determined by the sum of errors of ΔV_{FB}, d_{Na}, d_{BT} and $\frac{[Na]_{BT}}{[Na]}$ is estimated to be less than 100%.

Surface concentrations can be converted into volume concentrations provided (in coherence with profile measurements) that

$$C_{Na} = C_{Na\,ox} + \Delta C_{Na}\, e^{-x/L} \tag{6}$$

where C_{Na} is the volume concentration of sodium and x is the coordinate perpendicular to the surface

$$C'_{Na} = C_{Na\,ox} + \Delta C_{Na} \tag{7}$$

for $x = 0$ (at the $Si-SiO_2$ interface) and

$$C_{Na} = C_{Na\,ox} \tag{8}$$

for $x \gg L$ (in the oxide).
$L \approx 2$ nm as it can be seen in the figure.

The surface concentration will be expressed then as

$$[Na] = \int_0^{d_{ox}} C_{Na}\, dx = C_{Na}\, d_{ox} - L \Delta C_{Na}\, e^{-d_{ox}/L} + \Delta C_{Na} \cdot L \tag{9}$$

The surface accumulation of sodium can be determined from the profile measurement, too. We assume the sputtering rate to be equal in the oxide and the

transition layer (this is likely to be the case for chemical sputtering with oxygen in the chamber). On the figure it is to be seen:

$$\frac{C'_{\mathrm{Na}}}{C_{\mathrm{Na}}} \approx 40 \tag{10}$$

We also have to take into account that

$$L \Delta C_{\mathrm{Na}}\, e^{-d_{ox}/L} \approx 0 \tag{11}$$

because $d_{0x} \gg L$. So from expression (9)

$$C_{\mathrm{Na\,0x}} = \frac{[\mathrm{Na}]}{\mathrm{d}_{0x} - L + \frac{C'_{\mathrm{Na}}}{C_{\mathrm{Na\,0x}}} L} = 1{,}4 \cdot 10^{17}\ \mathrm{cm}^{-3} \tag{12}$$

This result is obtained exclusively on the basis of SIMS and BT stress measurements and is in good agreement with result obtained from neutron activation analysis [4].

The surface accumulation for a single layer can be estimated, too. Supposing that the above value of L (2 nm) is determined by the resolution of the SIMS measurements only, we can take $L' = 0.2$ nm and then

$$\frac{x'_{\mathrm{Na}}}{x_{\mathrm{Na}}} = \frac{C'_{\mathrm{Na}}}{C_{\mathrm{Na}}} \frac{L}{L'} \approx 400 \tag{13}$$

Where the molar fraction of sodium is denoted by x_{Na} as it is usual in the thermodynamics.

4. Thermodynamic calculation of the sodium accumulation on the Si—SiO_2 interface

The surface activity, i.e. the accumulation of a component at the surface (or interface) is well-known in the physics of fluids, however, it is not the case in the solid states physics [9].

In ref. [9] a simple theoretical treatment of surface accumulation has been described. According to that

$$\frac{x'_i}{x_i} = \exp\left(\frac{\gamma_1 - \gamma_i}{RT}\, \Phi_i\right) \tag{14}$$

where x_i is the molar fraction of the i-th component in a multicomponent system (x'_i is that on the surface), γ_1 and γ_i are surface free energies of the solvent and the solved matter, respectively, Φ_i is the partial molar surface of the i-th component and R is the universal gas constant. Expression (14) is a good approximation for nearly ideal solutions.

In the case of the sodium pile up on the Si—SiO_2 interface $\gamma_1 = \gamma_{Si/SiO_2}$ is the surface free energy of this interface, $\gamma_i \equiv \gamma_{Na}$ is the surface free energy of sodium and $\Phi_i \equiv \Phi_{Na} = 2.6 \cdot 10^4$ m^2 is the molar surface of sodium.

The problem is that no data are available in the literature for γ_{Si/SiO_2} and γ_{Na} (at room temperature).

The surface free energies of simple matters can be calculated in many cases on the basis of their surface free energies in liquid phase (γ_L) measured at the melting point (T_0). The calculation can be carried out according to the expression [10]

$$\gamma_L = \gamma(T_0)\left[1 + \frac{L_0}{(L_s L_p)^{1/2}} e^{L_0/3RT_0}\right] + \frac{d\gamma_L}{dT}(T - T_0) \tag{15}$$

Here L_0, L_s and L_p are the heats of melt, sublimation and evaporation, respectively.

The calculated data (for room temperature) are shown in the Table 1.

Table 1

Surface free energies

Material	γ [Jm^{-2}] measured	T_0 (°C)	Ref.	γ [Jm^{-2}] calculated
Si	1.230	1410	[11]	1.182
SiO_2	0.307	1300	[12]	0.345
Na	0.186	100	[13]	0.205

In the derivation of expression (15) providing quite accurate results (the mean deviation from the measured results at the melting point for 26 elements was less than 12%), it was supposed that

$$\frac{\gamma_{SL}}{\gamma_L} = \frac{\gamma_S}{\gamma_L} - 1 \tag{16}$$

It is supposed that this relation is valid in the more general case of interfaces, so that

$$\frac{\gamma_{Si/SiO_2}}{\gamma_{SiO_2}} = \frac{\gamma_{Si}}{\gamma_{SiO_2}} - 1 \tag{17}$$

From this relation $\gamma_{Si/SiO_2} = 0.837$ Jm^{-2}

By means of this value and that included in Table 1 one can evaluate expression (14):

$$\frac{x'_{Na}}{x_{Na}} \approx 680 \tag{18}$$

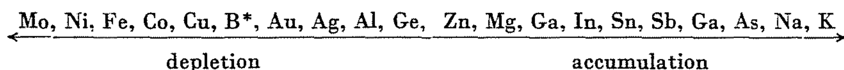
This value is in reasonable agreement with that obtained from the experiments

(expression (13)). It is to be noted that 10% error in the argument of expression (14) alters the final result by 80%.

The validity of Eq. (17) is not fully clear. The surface free energy calculated by it can be equal or greater than the real value. In principle, relation $\gamma_{Si/SiO_2} > 0$ is valid for the minimum possible value. But the observed sodium pile-up on the interface suggests that

$$\gamma_{Si/SiO_2} > \gamma_{Na} \tag{19}$$

A lot of free energy values have recently become known [10]. So, there is a possibility to compile an "accumulation series" on this base:



The surface free energies of elements are decreasing from the left to the right in this series. γ_{Si/SiO_2} obtained above lies between γ_{Ge} and γ_{Zn}. Every determination involving the accumulation or depletion of an element can be useful for verification of that value. Unfortunately accumulations of Na, K [3] and Sn [14] and the depletion of B [15] are only known in the present form of the "accumulation series". Pile-up of H, F, Cl [3], Li [4], Cs [14] and P [15] has also been detected at the $Si-SiO_2$ interface.

Therefore it seems to be important to seek further possibilities for the determination of the surface free energies of the materials mentioned before.

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Summary

Combined SIMS and electrical (BT) measurements were applied to analyse the Na content of thin MOS oxides. The evaluation elaborated here provides quantitative data and both surface and volume concentrations were determined. The accumulation of sodium on the $Si-SiO_2$ interface can be interpreted by the thermodynamical theory of surfaces applied to this case. There is a good qualitative agreement between the theoretical and measured accumulation ratios.

* The surface free energy of B is not known accurately, for $\frac{d\gamma_B}{dT}$ is unknown. An estimation could be made calculating with the mean value $\frac{d\gamma}{dT} = 0.2\,\frac{\gamma_S(T_0)}{T}$. So we obtain $\gamma_B = 1.37\ \mathrm{Jm^{-2}}$.

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