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# Diffusion of Sr, Bi, and Ta in amorphous SiO<sub>2</sub>

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### Abstract

Diffusion of Sr, Bi, and Ta in SiO<sub>2</sub> was studied to determine diffusion coefficients and diffusion mechanisms of these elements in the amorphous material. Technological motivation is the introduction of strontium bismuth tantalate (SBT) as ferroelectric material for nonvolatile memories. Diffusion from an SBT layer into a thin layer of SiO<sub>2</sub> was promoted by annealing at 800°C for times ranging from 1 to 24 h. Concentration profiles of the diffusing elements in the SiO<sub>2</sub> layer were recorded by secondary ion mass spectroscopy (SIMS). The measured profiles were compared to profiles derived from calculations for different diffusion mechanisms. The theoretical profile best matching the form of the measured profile was fitted to the experimental data, yielding information about the diffusion mechanism and the diffusion coefficient. The diffusion coefficient of Sr is in the range of  $10^{-15}$  cm<sup>2</sup>/s at 800°C and  $10^{-14}$  cm<sup>2</sup>/s for Bi. It was found out that Sr and Bi react with vacancies in the SiO<sub>2</sub>, forming fast-moving complexes. Tantalum shows no measurable diffusion in this time and temperature range. No information is available about the exact nature of the different Sr and Bi species, since SIMS can only detect elements but not their binding situation. Only indirect indications lead to the theory that vacancies play a role in the transformation from slow- to fast-moving species. Theoretical calculations of the behavior of the elements in SiO<sub>2</sub> may help to solve this problem.

Keywords: Sr; Bi; Ta; SBT; SiO<sub>2</sub>; Diffusion; SIMS

# 1. Introduction

Strontium bismuth tantalate  $(SrBi_2Ta_2O_9, SBT)$  is a new material in Si technology for storage capacitors in ferroelectric memory devices [1,2]. New materials may entail a risk in silicon processing [3] since they can introduce deep levels in the silicon band gap, cause precipitations, create additional charges in oxide, etc. [4]. Such effects have been reported to have a negative impact on device performance, reliability, and production yield [5]. Therefore, it is important to keep the new materials away from the active region of transistors etc. In many contamination studies, the primary concern has been the wafer backside, which may receive an unacceptably high contamination level from contami-

nated chucks or transport systems; for front-end-of-line processing, often no more than 10<sup>10</sup> cm<sup>-2</sup> are tolerated [6]. In order to be harmful, the contamination has to diffuse through the entire wafer thickness of  $> 600 \ \mu m$  to reach the active regions. In case of transition metals, the diffusion coefficient in Si is usually so large that this can occur even at low or moderate temperatures [4]. Sr, Bi, and Ta, however, were reported to exhibit low diffusion coefficients in Si [7]. Therefore, this contamination path appears to be of little importance for these elements. On the other hand, the ferroelectric film is present at the wafer front side at high concentrations  $(10^{17} \text{ cm}^{-2})$  and in micron-range distances from the active regions. Since the SBT capacitor is usually separated from the substrate by SiO<sub>2</sub>, diffusion in SiO<sub>2</sub> is of main importance to assess whether SBT elements can reach the active device.

Ferroelectric SBT is a bismuth-layered perovskite, a so-called Aurivillius-phase, in which two perovskite layers are sandwiched between bismuth-oxide layers

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[1,8]. This phase appears after annealing at temperatures above  $700^{\circ}$ C. Below this temperature, SBT exists in a fluorite-like phase, whereas directly after spin-on deposition it is mostly in an amorphous state [9].

Diffusion coefficients and mechanisms for many elements in crystalline materials such as silicon are well established [4,10]. Silicon dioxide is not as well defined as single-crystalline silicon. The SiO2 network consists of SiO<sub>4</sub> tetrahedra with a Si atom in the middle and shared O atoms at the corners, connecting the tetrahedra. Thus, there is a short-range order, but no long-range order since the tetrahedra are randomly spaced, allowing a variety of bond angles and some distribution of bond lengths [11]. Due to the short-range order, point defects such as vacancies or self-interstitials can be defined in amorphous SiO<sub>2</sub> as in a crystalline material. The random order is responsible for a large fraction of "free volume", i.e. empty space between atoms, which corresponds to the interstitial sites in crystalline solids. Interstitial diffusion mechanisms, therefore, appear to be dominant in amorphous materials. On the other hand, some elements such as B are known to diffuse primarily on substitutional "lattice" sites [12]. SiO<sub>2</sub> properties, e.g. hydrogen content or vacancy concentration depend on the method of deposition and history of the sample [13]. Diffusion behavior strongly depends on these properties and the conditions during diffusion, causing differences of several orders of magnitude in diffusion constants for the same element [14]. Diffusion coefficients of dopants such as B, Al, P, As, and Sb have been established because of their technological importance [14]. Diffusion studies in SiO<sub>2</sub> are also available for Fe [15-17], Cu [15,18], Ag [18,19], Au [18,20], Ti [18,21], Pd [18], Co [21], Ni [22], and Cr [15].

Secondary ion mass spectroscopy (SIMS) is particularly well suited for diffusion studies because, in general, it can record concentration profiles with depth resolution and detection limits unmatched by other analytic techniques. SIMS diffusion profiles allow extraction of the diffusion constants, and the form of the profiles yields valuable information about the diffusion mechanism.

## 2. Experimental

500 nm thick SiO<sub>2</sub> films were deposited on Si wafers by plasma-enhanced chemical vapor deposition (PECVD) from tetraethylorthosilicate (TEOS) in an applied materials precision 5000 reactor at 390°C and densified by subsequently annealing at 900°C for 1 h under N<sub>2</sub> atmosphere. The properties of this oxide were described by Nguyen et al. [23].

On top of the oxide a 90 nm thick SBT film was deposited by a spin-on technique from metalorganic precursors which was dried on a hot plate at 260°C,

followed by a rapid thermal processing (RTP) step at  $750^{\circ}$ C for 30 s. Some samples underwent a so-called ferro-anneal at  $800^{\circ}$ C for 1 h in O<sub>2</sub> atmosphere in order to crystallize the SBT in the ferroelectric phase. Since diffusion studies on samples with and without ferro-anneal showed little difference [24], in this publication only samples without ferro-anneal are mentioned.

On all samples a 500 nm thick  $SiO_2$  layer was deposited by the same PECVD step as before but without densification.

Some samples were prepared in the same way but without the precursors containing bismuth and tantalum. In this way, a source layer containing only strontium with a thickness of 100 nm was obtained and then covered by an oxide layer as described. A schematic cross section of the samples is shown in Fig. 1.

Then the wafers were quartered and the pieces underwent an anneal to promote diffusion. It was carried out in a furnace that allowed annealing at 800°C for times ranging from 1 to 24 h. Diffusion during heating and cooling times was accounted for by modifying the times used later for calculation of diffusion coefficients.

SIMS was used to measure depth profiles. All measurements were carried out in a CAMECA ims6f system using  $O_2^+$  5 keV primary ions for detection of Sr<sup>+</sup>, Bi<sup>+</sup>, and Ta<sup>+</sup> secondary ions, respectively. Charging effects caused by the insulating oxide were compensated by supplying electrons of 8 keV initial energy. Additionally, the surfaces of all samples had been covered with a thin AuPd contact layer to improve the compensation. To eliminate undesired interferences, a mass resolution in the range of 2100–2400 for  $m/\Delta m$  was applied. The resulting detection limits were ~2 × 10<sup>14</sup>, ~7 × 10<sup>14</sup>, and ~2 × 10<sup>15</sup> cm<sup>-3</sup> for Sr<sup>+</sup>, Bi<sup>+</sup>, and Ta<sup>+</sup>, respectively.

In order to determine the diffusion mechanism, theoretical concentration profiles were calculated for different mechanisms and fitted to the experimental data. The profile best fitting the data determines the diffusion mechanism, the fit parameters allow calculation of the diffusion coefficient. The mechanisms that



Fig. 1. Cross section of the samples (schematic). In some samples, SBT was replaced by a layer containing only strontium (Section 6).

occur in this publication are described in the following section.

#### 3. Theory

Diffusion is governed by Fick's second law

$$\frac{\partial C_{\rm M}}{\partial t} = D \frac{\partial^2}{\partial x^2} C_{\rm M} \tag{1}$$

with the time- and space-dependent concentration  $C_{\rm M}$  of the diffusing species, the diffusion coefficient *D*, time *t* and space coordinate *x*. It is shown here in onedimensional form since all diffusion profiles in this work are one-dimensional. *D* is usually a second-order tensor. But since amorphous SiO<sub>2</sub> consists of a random network, there are no crystal orientations, the material is isotropic. Therefore *D* is reduced to a scalar quantity.

The solid layer of SBT can be considered to be an infinite source of diffusing material M, so the concentration at the interface  $C_0$  remains constant throughout the diffusion process, leading to the boundary condition

$$C_{\rm M} = C_0 \quad \text{at } x = 0, \ t > 0$$
 (2)

with the interface at x = 0 and diffusion proceeding in the positive direction.

At the beginning of the anneal, the top  $SiO_2$  layer is still free of diffusing material, so the initial condition is

$$C_{\rm M} = 0$$
 at  $x > 0, t = 0.$  (3)

The solution of Eq. (1) under these conditions is given by [25]

$$\frac{C_{\rm M}}{C_0} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right),\tag{4}$$

where erfc stands for the complementary error function.

In some samples, this solution did not fit the experimental profiles. There appears to be a loss of diffusing material. This loss can occur by a reaction of the diffusing species with the matrix or with point defects in the  $SiO_2$ . Since SIMS cannot tell apart different species of the same element, the reaction product has to diffuse away quickly, otherwise the SIMS profile would be unchanged by the reaction. If P is the point defect, the reaction can be described by

$$M_{slow} + P \xrightarrow{\kappa_f} MP_{fast}.$$
 (5)

 $R_{\rm f}$  is the reaction constant. In this case, M disappears with a rate proportional to the concentration of M and P as

$$\frac{\partial C_{\rm M}}{\partial t} = -R_{\rm f} C_{\rm M} C_{\rm P} = -R C_{\rm M} \quad \text{with } R = R_{\rm f} C_{\rm P}. \tag{6}$$

 $C_P$  stands for the concentrations of P. This term must be added to Eq. (1) and yields the solution [25,26]

$$\frac{C_{\rm M}}{C_0} = \frac{1}{2} \exp\left(-x\sqrt{\frac{R}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{Rt}\right) + \frac{1}{2} \exp\left(x\sqrt{\frac{R}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{Rt}\right).$$
(7)

Without reaction, i.e. for R = 0, this simplifies to Eq. (4). On the other hand, for long times or large R, an equilibrium between material consumed by the reaction and material transported by diffusion is reached and Eq. (7) simplifies to a time-independent expression

$$\frac{C_{\rm M}}{C_0} = \exp\left(-x\sqrt{\frac{R}{D}}\right).\tag{8}$$

# 4. Strontium

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Fig. 2 shows strontium profiles after diffusion from an SBT layer. The diffusion profiles broaden with increasing time, the concentration at the interface stays constant as required by Eq. (2). The best fit was obtained for a model including diffusion and an additional reaction as described by Eq. (7). The calculated values for D and R are shown in Table 1 and Fig. 3. The diffusion coefficient D stays nearly constant, only a slight decrease is observed over time that can be explained by annealing of the SiO<sub>2</sub> [27].

The reaction rate, however, decreases by more than an order of magnitude. As shown in Eq. (6), the reaction rate is the product of the reaction constant and the concentration of the reactants. It is known that the concentration of vacancies in the oxide decreases during

no anneal



Fig. 2. Strontium concentration profiles in SiO<sub>2</sub> after diffusion from an SBT layer during anneal at  $800^{\circ}$ C for the indicated times. The black solid lines are the fits following Eq. (7).

Table 2

Table 1 Strontium diffusion coefficient and reaction rate after diffusion from an SBT source

Temperature (°C)	Time (h)	Diffusion coefficient (cm <sup>2</sup> /s)	Reaction rate $(s^{-1})$
800	1	$\begin{array}{c} 8.7 \times 10^{-16} \\ 8.6 \times 10^{-16} \\ 5.0 \times 10^{-16} \end{array}$	$1 \times 10^{-4}$
800	4		$8 \times 10^{-5}$
800	24		$1 \times 10^{-5}$



Fig. 3. Diffusion coefficient (circles, left scale) and reaction rate (squares, right scale) of strontium after diffusion from an SBT source at  $800^{\circ}$ C.

the anneal [23], therefore the decrease of the reaction rate can be explained if a vacancy is assumed to be the reaction partner of the diffusing strontium

$$Sr_{slow} + V \Rightarrow SrV_{fast}.$$
 (9)

The strontium species from the SBT source,  $Sr_{slow}$ , reacts with a vacancy V in the  $SiO_2$  to form a fastmoving complex,  $SrV_{fast}$ . This complex diffuses away and accumulates at the surface or interface. But the strontium concentration at the surface is too high to be explained exclusively by accumulation of complexes. Some of it is due to contamination from the outside. Contamination tests showed similar concentrations on clean wafers that did not contain any strontium and have been annealed with these samples.

# 5. Bismuth

Bismuth profiles after diffusion from an SBT source are shown in Fig. 4. As for strontium, the concentration at the interface remains constant. The best fit for these profiles is obtained by Eq. (8). This means that diffusing bismuth reacts with the matrix to form another species that diffuses away quickly. Although this equation is time-independent, the slope of the exponential profiles



Fig. 4. Bismuth concentration profiles in  $SiO_2$  after diffusion from an SBT layer during anneal at  $800^{\circ}C$  for the indicated times. The black solid lines are the fits following Eq. (8).

Bismuth fit parameter after diffusion from an SBT source (see text for details)

Temperature (°C)	Time (h)	$(R/D)^{1/2}$ (cm <sup>-1</sup> )
800	1	$2.8  imes 10^5$
800	4	$1.9  imes 10^5$
800	24	$1.1 \times 10^{5}$

changes for different diffusion times. This means that the term  $(R/D)^{1/2}$  in Eq. (8) decreases. This decrease can easily be explained if bismuth reacts with vacancies just as strontium

$$Bi_{slow} + V \Rightarrow BiV_{fast}.$$
 (10)

When the concentration of vacancies decreases, the reaction rate R decreases as well.

The same behavior is observed for bismuth in crystalline silicon, where it forms complexes with vacancies that diffuse faster than substitutional bismuth [28]. Unfortunately this equation does not allow the separate calculation of D and R. The parameter  $(R/D)^{1/2}$  is shown in Table 2. It is possible to estimate the diffusion coefficient for bismuth. This leads to a value of  $D_{\rm Bi} \approx 1 \times 10^{-14}$  cm<sup>2</sup>/s, i.e. one order of magnitude faster than strontium. The high concentrations of bismuth near the surface are mostly due to contamination during the anneal.

## 6. Interaction of strontium and bismuth

Fig. 5 shows strontium concentration profiles from a bismuth-free strontium source that has been annealed in the same way as the samples that are shown in Fig. 2.



Fig. 5. Strontium concentration profiles in SiO<sub>2</sub> after diffusion from an strontium layer during anneal at  $800^{\circ}$ C for the indicated times. Comparison with Fig. 2 shows broader profiles and consequently faster diffusion than from an SBT source.



Fig. 6. Tantalum concentration profiles in SiO<sub>2</sub> after diffusion from an SBT layer during anneal at 800°C for the indicated times. The figure shows only the interface region in a stretched representation, the inset shows the complete profiles. No measurable diffusion can be observed.

The exact form of the profiles is of no importance in this paper and is discussed elsewhere [29]. Comparison of the two figures shows that strontium diffuses much faster from the strontium source than from the SBT source, leading to broader profiles. This is another indication for the theory developed in the previous sections: both elements react with vacancies to form fast-diffusing complexes. If both diffuse together, the bismuth concentrations shown in Fig. 3 are higher than the strontium concentrations in Fig. 2. As a result, bismuth takes away most of the vacancies, leaving only few for strontium to react. On the other hand, if strontium diffuses alone, it can react with all the vacancies available to form the fast-moving complex, which leads to a faster diffusion. Thus, if both elements diffuse together, bismuth slows down the diffusion of strontium. The diffusion coefficients mentioned in Table 1 are for diffusion from an SBT source, i.e. when both elements are present.

## 7. Tantalum

Concentration profiles for tantalum after diffusion from SBT are shown in Fig. 6. The inset shows the complete profiles, the main part of the figure shows the interface region of these profiles. Even in this enlarged representation, the profiles hardly differ. Therefore, no fits are possible and no diffusion coefficient can be calculated. It is possible to calculate an upper limit for the tantalum diffusion coefficient by trying to fit Eq. (4) to the profiles. This leads to the result  $D_{\text{Ta}} \leq 1 \times 10^{-17} \text{ cm}^2/\text{s}$ , i.e. two or three orders of magnitude lower than strontium or bismuth, respectively.

## 8. Summary

Diffusion of strontium, bismuth, and tantalum from an SBT source in SiO<sub>2</sub> has been investigated. The experimental profiles can be explained if, in addition to diffusion, a reaction of strontium and bismuth with vacancies in the SiO2 is taken into account similar to the behavior of bismuth in crystalline silicon. This explanation is supported by the fact that strontium diffuses faster if no bismuth is present. Bismuth slows down the strontium diffusion by taking away the vacancies needed to form the fast-moving strontium species. The diffusion coefficient of strontium from SBT is in the order of 1  $\times$  $10^{-15}$  cm<sup>2</sup>/s, the diffusion coefficient of bismuth cannot be calculated exactly, but estimated to be about  $1 \times$  $10^{-14}$  cm<sup>2</sup>/s. Tantalum diffusion is too slow to be measured in these experiments; the diffusion coefficient is below  $10^{-17} \text{ cm}^2/\text{s}$ .

Diffusion coefficients of strontium and bismuth are high enough to be a risk for active devices. Therefore, a diffusion barrier around the SBT layer will be necessary in ferroelectric memory devices.

Open questions include the direct detection of the vacancy complexes as well as the study of their exact nature. It is also important to find and examine suitable materials for the diffusion barrier.

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