Direct micro-imaging of point defects in bulk SiO_2, applied to vacancy diffusion and clustering

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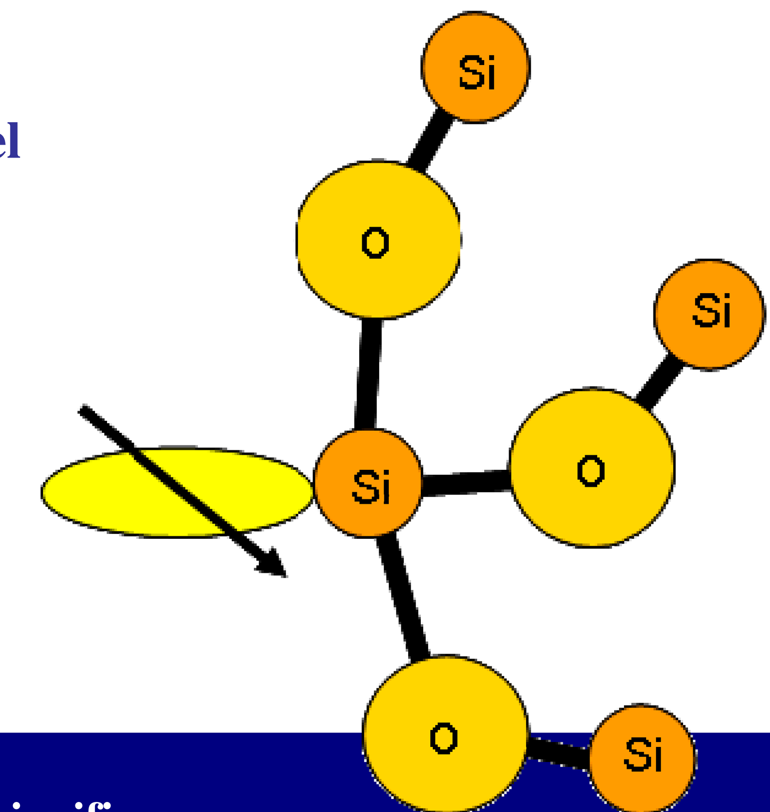

Abstract

Electron spin resonance microscopy (ESRM) was employed in the evaluation of diffusion characteristics of point defects (E′ paramagnetic centers) in amorphous SiO_2. Samples were subjected to inhomogeneous ɣ-irradiation creating a heterogeneous distribution of E′-centers in SiO_2 substrates. The samples were measured by ESRM after preparation and following several heat treatment cycles. These measurements revealed pronounced changes in the distribution of the E′-centers due to the heat treatments. The defects' reorganization did not obey simple diffusion laws and they exhibited an attraction towards areas with higher initial concentration. This behavior was simulated by an empirical model, resulting in the evaluation of the defects' diffusion constant, its activation energy, and their characteristic attractive potential. This is the first time that ESR imaging is employed to directly obtain such type of fundamental information regarding the diffusion behavior and interaction of point defects.

E' - centers

In a flawless SiO_2 structure, an oxygen (O) atom is bonded to the Si atoms, and acts as a bridge between two SiO_4 tetrahedra. An oxygen vacancy in place of a bridging atom is a source of intrinsic point defects. The most frequently encountered oxygen vacancy related point defect is the E' center, which is characterized by an unpaired electron localized in a sp-hybrid orbital of the silicon atom bonded to three oxygen atoms.

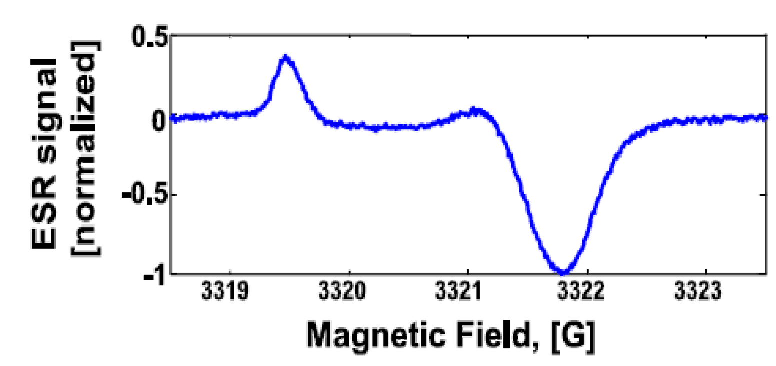

Fig 1. E' center CW ESR spectrum.

E' centers significance

Play a dominant role in the degradation of Si/SiO_2 based devises. For example, they are the main source for oxide leakage currents.

The performance of optical devices made from SiO_2, is strongly influenced by the presence of point defects, which cause a reduction in transparency of the material.

Motivation

Point defect diffusion and clustering plays a crucial role in many aspects of semiconductor devices. The capacity to control device profiles is crucially dependent on the ability to model in a quantitative way the motion and annealing of point defects. This type of information is also important, for example, in numerical programs dealing with device-processing simulation.

In this work we are measuring the diffusion of defects, trying to generate a "step function" in their concentration and subsequently monitoring their reorganization under controlled temperature and time. We directly monitor the point defects them selves by employing a state-of-the-art ESR micro-imaging technique. This is done in order to image defects in amorphous SiO_2 with a resolution that is sufficient to observe their unique diffusion behavior (including mutual interaction) and also estimate the diffusion activation energy.

Experimental System

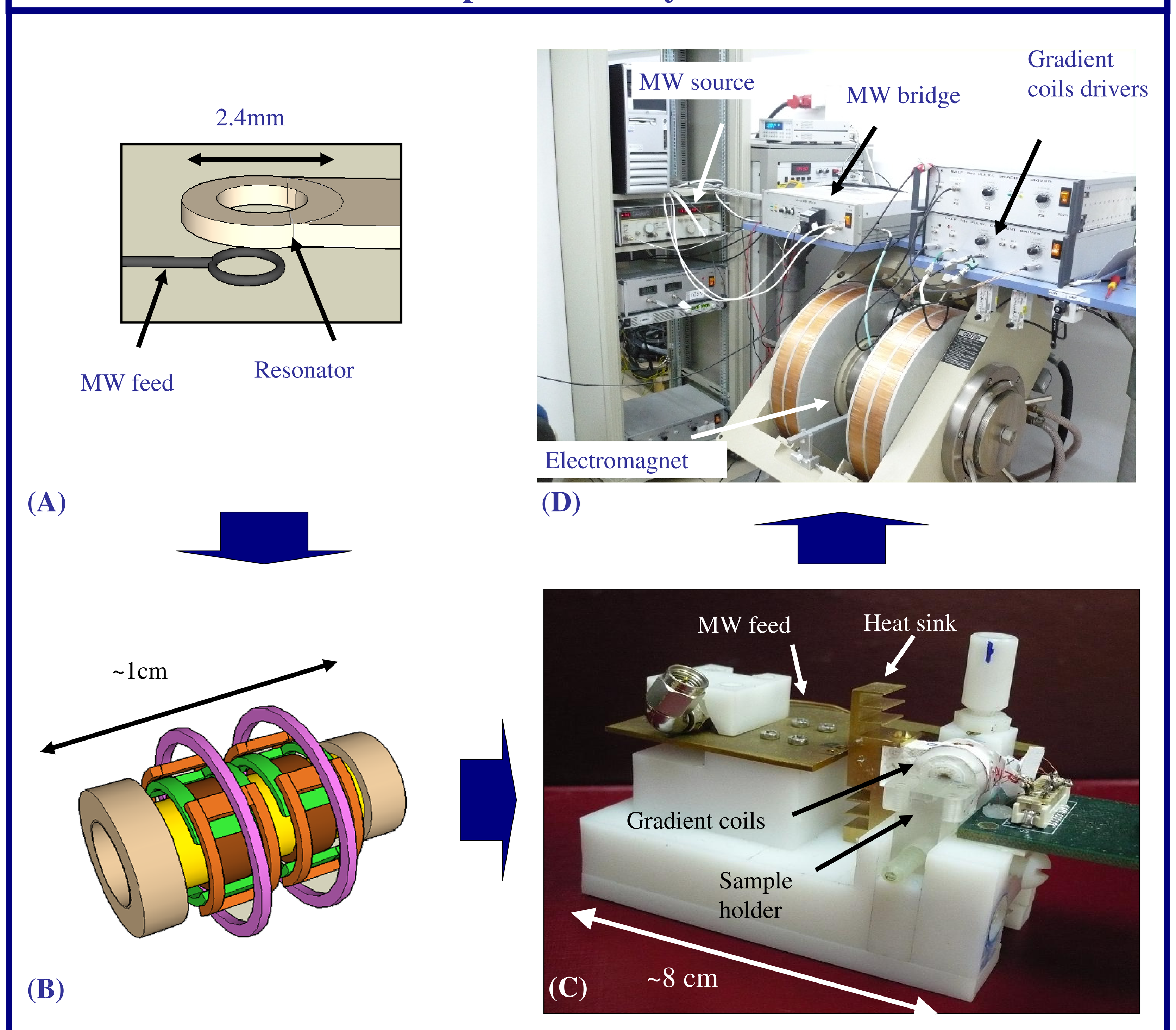

Fig 2. ESRM experimental system. (A) MW dielectric resonator (TiO_2) coupled to MW feed. The sample is placed in the middle of the resonator ring. (B) Gradient coil construction ((A) is inside (B)). (C) ESRM imaging probe. (D) General view of the system.

γ irradiation of SiO_2 samples

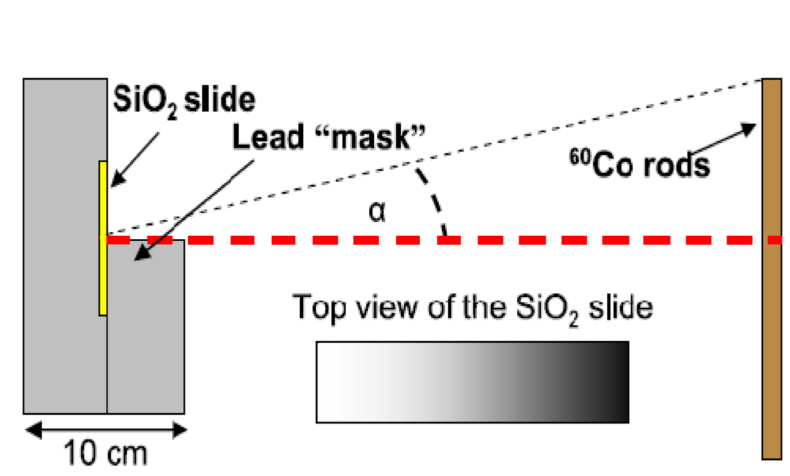

Fig 3. The experimental set-up used for generating a gradient of paramagnetic defects in the SiO_2 slide. The top view of the slide shows the ideal distribution of defects following such kind of irradiation.

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Experimental Results

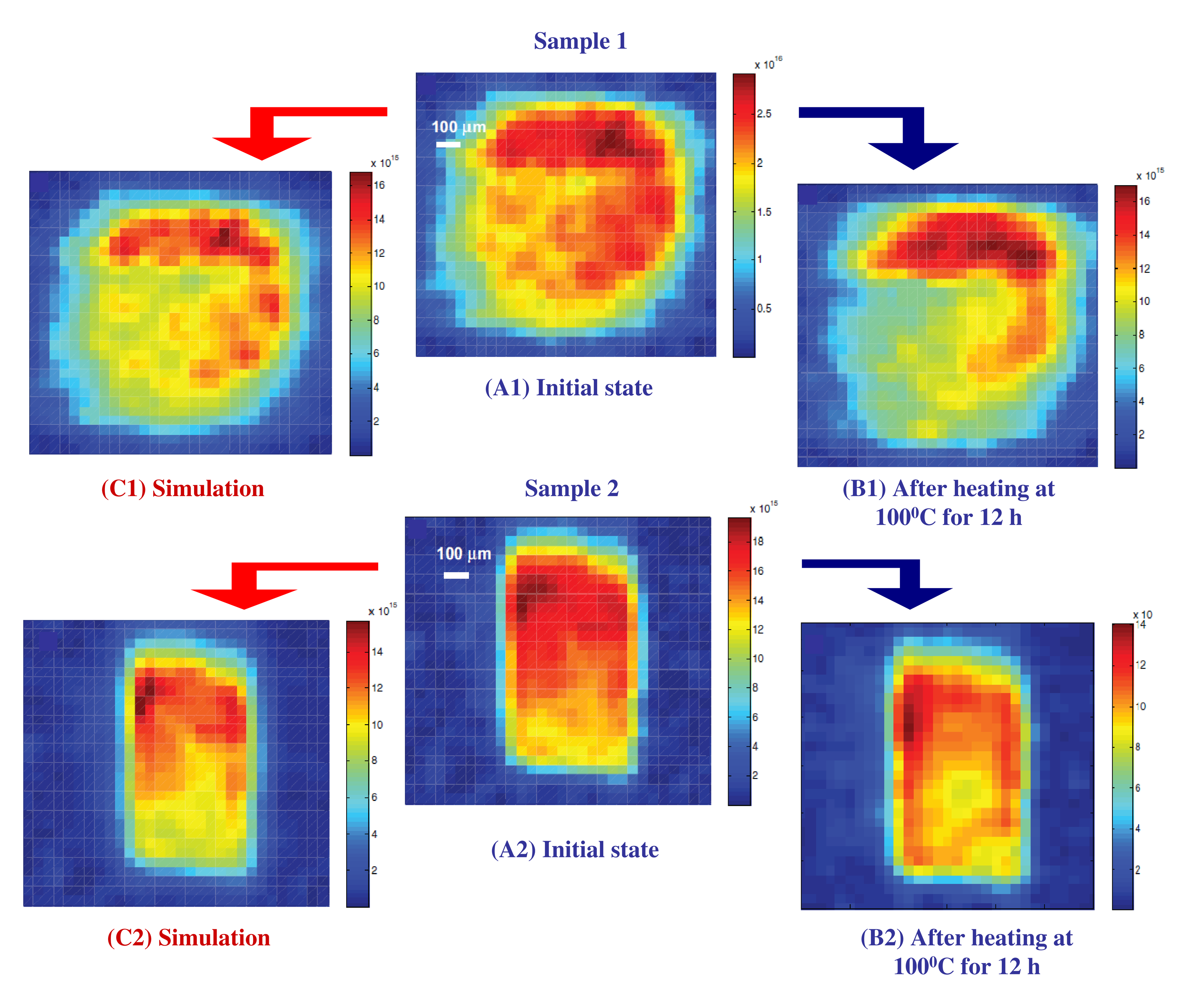

Fig 4. Experimental results vs. simulation for two samples. (A1)&(A2) ESR image covering part of SiO_2 sample taken after the irradiation. (B1)&(B2) ESR image of the sample after the heat treatment. (C1)&(C2) Simulated result based on the initial state (A1)&(A2). The vertical color scale represents the concentration of defects in arbitrary scale.

Theoretical Model

The flux of defects in the presence of concentration gradient and force is described by the Fokker – Planck equation:

$$J_{\vec{r}} = -D \cdot \frac{\partial C}{\partial \vec{r}} + D \cdot C \cdot \frac{F_{\vec{r}}}{k_B T}$$

$J_{\vec{r}}$ - Flux of defects.

D - Diffusion constant.

C - Defect concentration.

$\vec{r}$ - Distance vector along the direction for which the flux and force are calculated.

$F_{\vec{r}}$ - Force

k_B - Boltzmann constant.

T - Temperature

The force is assumed to behave according to the following empirical expression: $F_{\vec{r}} = k_F \cdot C_i \cdot C_j \cdot \left|\vec{r}_i - \vec{r}_j\right|^{-4}$

k_F - Force constant.

C_i & C_j - Concentration of defects in two different locations.

$\left|\vec{r}_i - \vec{r}_j\right|$ - Distance between these two different locations.

Evaluated parameters

	D (m^2/s)	k_F ($J \cdot m^7$)	E (eV)
Sample 1	$4 \cdot 10^{-15}$	$0.17 \cdot 10^{-64}$	0.16
Sample 2	$4.1 \cdot 10^{-15}$	$0.25 \cdot 10^{-64}$	0.24

Table 1. Summary of the experimental and simulated results. Constant values, calculated using the proposed empirical model.