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Diffusion of germanium in silica glass

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Abstract

The first measurements of the diffusion coefficient of substitutional germanium in silica glass are reported. Samples were prepared by implanting germanium ions into high purity silica. The concentration of germanium at the surface remained essentially zero, indicating that germanium evaporated readily from the surface of the sample. It was found that, during an initial anneal, the peak concentration of germanium shifted toward the surface. We attribute this to a drift motion of ions in the field created by the implant. The motion of the ions during an anneal could be changed by applying a DC electric field. A preliminary annealing procedure was established which eliminated the drift motion, so that the subsequent motion of germanium could be described as simple diffusion. EXAS measurements indicated that germanium was clustered together in the as-implanted samples, but that after this pre-anneal, germanium was incorporated into the matrix. The diffusion coefficient of the substitutional germanium in silica was found to be $7250\exp(-6.6\times10^4/T)\ \mathrm{cm^2/s}$, which corresponds to an activation energy, $Q = 131$ kcal/mol.

1. Introduction

Diffusion in silica glass has been a subject of much study since there are a variety of diffusion mechanisms for various diffusing species. There are species which diffuse through the glass without modifying the structure of the matrix, and these are called non-interacting [1,2]. There are both interstitial and substitutional non-interacting species. Species which modify the structure of the glass matrix are called interacting species [3].

Nitrogen is an example of a non-interacting interstitial species. It diffuses interstitially through silica without modifying the matrix. Diffusion is very rapid for interstitial elements, and their diffusivity depends on the openness of the matrix and the molecular size of the diffusing species.

Germanium, the dopant used in this study, is an example of a non-interacting substitutional species. Since it has similar bonding characteristics to silicon, germanium can replace silicon in the matrix of the glass, without significantly changing the network structure. Substitutional non-interacting elements diffuse much more slowly than interstitial elements.

In contrast, ionic species such as sodium, for example, are interacting. They change the network structure of the silica matrix so that its physical properties, such as the electrical conductivity, are altered. The diffusivity of these elements depends strongly on their concentration changing the diffusivity of other elements.

2. Experimental procedure

Silica glass GE224 was selected for this research because of its high purity and low OH^- content [4]. Germanium was implanted into silica at an energy of 170 keV to a dose of 5×10^{16} ions/cm^2. The end of range is at approximately 1200 Å.[1] The surface of the glass was flame polished prior to implantation, in order to

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[1] Implantation performed by Implant Sciences of Boston, MA.

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reduce the possibility of surface nucleation and crystallization. An open ended alumina tube furnace which was resistively heated by platinum wire was constructed for these experiments. The samples were placed on end in platinum boats and inserted into the furnace for the desired annealing period. The distribution of germanium in the samples was determined using Rutherford backscattering (RBS) at the particle beam laboratory in the Physics Department at the University of Arizona.

2.1. Germanium quantum dots

There have been several studies of germanium which have been implanted or otherwise incorporated into silica in order to fabricate quantum dots [5–12]. In these studies, small precipitates of semiconducting germanium are prepared in an insulating silica matrix in order to study their optical properties. Electrons, which are confined in the germanium precipitates by the surrounding insulating silica matrix, have optical properties which depend on quantum confinement effects, which is why the precipitates are called quantum dots.

In order to produce quantum dots, germanium-containing silica thin films are annealed in a reducing atmosphere to avoid oxidation of germanium, and to precipitate nanoclusters of semiconducting germanium. The annealing temperature and atmosphere are designed to prevent germanium from incorporating into the matrix. In an oxygen deficient environment, as is created by the reducing atmosphere, the oxygen in the silica preferentially stays with the silicon, and so germanium is not incorporated into the matrix.

When an excess of oxygen is present, oxygen combines with germanium and incorporates into the silicon oxide matrix as germanium oxide. The diffusion of germanium ions in a reduced oxygen environment is expected to be quite different than in the presence of excess oxygen.

2.2. Incorporation of germanium into a silica matrix

Since the purpose of this research was to measure the diffusion of substitutional germanium in silica it was critical to be certain that germanium clusters were not forming in the glass. The RBS analysis technique cannot distinguish between germanium nanoclusters and germanium which is substitutional in the matrix [13]. To determine if clusters were forming, a variety of techniques were used including TEM, fluorescence spectrometry, Raman spectrometry, X-ray diffraction, and edge X-ray absorption spectrometry (EXAS). The only technique that produced conclusive results was EXAS, which was carried out at the Stanford Linear Accelerator Center (SLAC).

The EXAS spectrum of the germanium ions in an as-implanted sample, Fig. 1, is dominated by a peak at

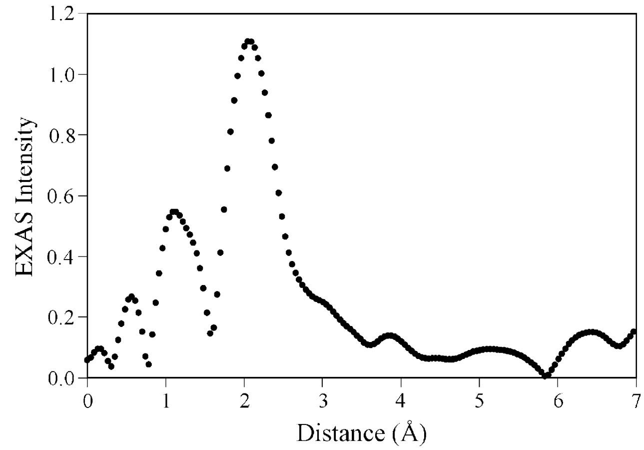

Fig. 1. EXAS spectra of germanium in an as-implanted sample. The intensity indicates the location of other atoms near germanium atoms. The peak at 2.1 Å corresponds to the Ge–Ge distance. The germanium atoms are surrounded by other germanium atoms, which indicates that the germanium atoms are clustered in the as-implanted sample.

2.1 Å which corresponds to Ge–Ge separation [14]. This indicates that the germanium atoms in the as-implanted sample are clustered together, and surrounded by other germanium atoms. The spectrum of a sample which was annealed in air for 30 min at 1300 °C, Fig. 2, is quite different. It is dominated by a peak at 1.3 Å, which corresponds to Ge–O separation [15]. This indicates that germanium atoms are surrounded by oxygen after the 30 min anneal at 1300 °C. The data in Fig. 2 indicates that germanium is fully incorporated into the glass matrix during the anneal.

2.3. Diffusion experiments

The concentration of germanium at the surface of the glass was found to be zero after all annealing treatments

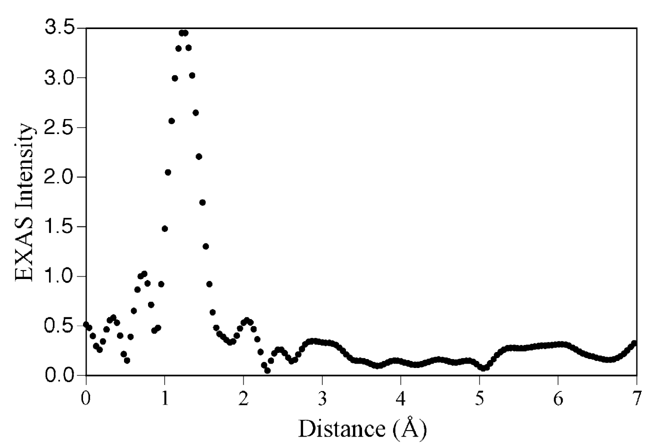

Fig. 2. EXAS spectra of germanium after a 30 min anneal in air at 1300 °C. This is the pre-treatment anneal discussed. The spectrum is now dominated by a peak at 1.3 Å, which corresponds to the Ge–O distance. The germanium atoms are now surrounded by oxygen atoms, indicating that germanium has been incorporated into the glass matrix.