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Equilibrium concentration of oxygen rich and deficient defect centers in germanosilicate glasses

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Abstract

Equilibrium concentrations of oxygen rich and deficient defect centers are calculated as a function of temperature and glass redox condition for germanosilicate glasses. We have here used the approach of Silin and Lace [J. Non-Cryst. Solids 149 (1992) 54–61] but extended it to include the case of binary system of germanosilicate glasses. A set of 23 reactions is identified as the possible pathway for formation of different defect centers. Each of these reactions are represented by forward and backward steps with Arrhenius kinetics and their activation energies are estimated based on the relevant bond energies of the involved species. Equilibrium concentrations are determined by setting rates of each of these reactions equal to zero. Typical results are presented for glasses which are: (i) stoichiometric, (ii) glasses with excess oxygen levels of 10^{16} to 10^{20} cm^{-3}, and (iii) glasses which are oxygen deficient by 10^{16} to 10^{18} cm^{-3}.

1. Introduction

Defects and structural imperfections in silica and doped silica glasses have been extensively studied. Understanding of the origin of these defects and the ability to predict their concentration is critical for a number of applications. These include performance of microelectronic devices [22], optical fiber communications, photosensitivity of silica [28], photosensitivity of germania doped silica [31], photoinduced Bragg gratings [12,13,17], photorefractive effect, second harmonic generation [11], nonlinear transmission properties of optical fibers [16], formation of draw induced defects in optical fibers [1,20], design of metal oxide semiconductor devices [3,30], etc. A number of theoretical and experimental studies have been carried out to identify the structure of these defects and the mechanism of their formation and healing. Various defect centers in silica and germanosilicate glasses have recently been reviewed in [25,21]. Quantum-chemical calculations, molecular orbital methods and density functional theory calculations have been carried out to understand the behavior of these defects theoretically [4,28–30]. Electron spin resonance, cathodoluminescence, photoluminescence, emission/absorption and other spectroscopic methods have been used to characterize these defects in germanosilicate glasses [1,2,7,26,27,18,19].

We here present a model to predict the equilibrium concentrations of intrinsic oxygen rich and deficient defect centers in germanosilicate glasses. We have used the approach of Silin and Lace [24] but have extended it to include the case of binary system of germanosilicate glasses. A set of 23 reactions are identified as the possible pathway to forming these defects. Each of these reactions are represented by forward and backward steps with Arrhenius kinetics and their activation energies

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are estimated based on the relevant bond energies of the involved species. Equilibrium concentrations are determined by setting reaction rates of each of these reactions equal to zero.

2. Reaction mechanism and reaction rates

We consider that the glass is comprised of germania–silica network having total site concentration of N_T ($=2.2\times10^{22}$ cm^{-3}). Depending on the germania content in the glass, a fraction of these sites (N'_R) are germania–silica network, while the rest (N_R) are silica–silica network. Before writing the reaction mechanism of formation of different defect centers, notation for defects and activation energy is defined below:

Network sites and defect center notation

N_R concentration of ≡Si–O–Si≡ network
N'_R concentration of ≡Si–O–Ge≡ network
N_T $N_R + N'_R = 2.2\times10^{22}$ cm^{-3}
n_a concentration of ≡SiO$^\bullet$ (Si non-bridging oxygen hole center)
n_b concentration of ≡Si$^\bullet$ (Si E' centers)
N_A concentration of ≡Si–O–O–Si≡ (Si–Si peroxy linkage)
N_B concentration of ≡Si–Si≡ (oxygen vacancy, metal–metal bond)
N_r concentration of ≡Si–O–O$^\bullet$ (Si peroxy radical)
N_s concentration of =Si$^\bullet$ (twofold coordinated silicon atom)
n'_a concentration of ≡GeO$^\bullet$ (Ge non-bridging oxygen hole center)
n'_b concentration of ≡Ge$^\bullet$ (Ge E' centers)
N'_A concentration of ≡Si–O–O–Ge≡ (Si–Ge peroxy linkage)
N''_A concentration of ≡Ge–O–O–Ge≡ (Ge–Ge peroxy linkage)
N'_B concentration of ≡Si–Ge≡ (oxygen vacancy, metal–metal bond)
N''_B concentration of ≡Ge–Ge≡ (oxygen vacancy, metal–metal bond)
N'_r concentration of ≡Ge–O–O$^\bullet$ (Ge peroxy radical)
n_{O_2} concentration of molecular oxygen
n_O concentration of atomic oxygen

Bond energy notation

E_O molecular oxygen bond energy
E_d atomic oxygen diffusion activation energy
E bond energy of Si–O bond
E_B bond energy of Si–Si bond
E_G bond energy of Ge–O bond
E'_B bond energy of Si–Ge bond
E_A bond energy of O–O bond
E''_B bond energy of Ge–Ge bond
E_s activation energy to generate ≡Si–Si≡ from =Si$^\bullet$

Each reaction is considered to be reversible with forward and backward steps, which follow Arrhenius kinetics. The activation energies are estimated from bond energy considerations, while the pre-exponential constants in the Arrhenius expression (or the frequency factor ω) for the backward and forward steps for each reaction are considered to be equal. Thus the kinetic rate expressions are written in terms of dimensionless time. $\tau = \omega t$. Following the approach of Silin and Lace [24] for silica glasses, we propose the following mechanism for germanosilicate glasses:

Reaction 1

$$O_2 \leftrightarrow O + O \tag{1}$$

$$\frac{dn_{O_2}}{d\tau} = -n_{O_2} e^{-(E_0+E_d)/kT} + n_O \frac{n_O}{N_T} e^{-E_d/kT}.$$

Reaction 2

$$\equiv Si–O–Si\equiv \leftrightarrow O + \equiv Si–Si\equiv \tag{2}$$

$$\frac{dN_R}{d\tau} = -N_R e^{-2E/kT} + N_B \frac{n_O}{N_T} e^{-E_B/kT}.$$

Reaction 3

$$\equiv Si–O–Ge\equiv \leftrightarrow O + \equiv Si–Ge\equiv \tag{3}$$

$$\frac{dN'_R}{d\tau} = -N'_R e^{-(E+E_G)/kT} + N'_B \frac{n_O}{N_T} e^{-E'_B/kT}.$$

Reaction 4

$$\equiv Si–O–Si\equiv \leftrightarrow \equiv Si^\bullet + {}^\bullet O–Si\equiv \tag{4}$$

$$\frac{dN_R}{d\tau} = -N_R e^{-E/kT} + n_a \frac{n_b}{N_T}.$$

Reaction 5

$$\equiv Si–O–Ge\equiv \leftrightarrow \equiv Si^\bullet + {}^\bullet O–Ge\equiv$$

$$\frac{dN'_R}{d\tau} = -N'_R e^{-E/kT} + n'_a \frac{n_b}{N_T}. \tag{5}$$

Reaction 6

$$\equiv Si–O–Ge\equiv \leftrightarrow \equiv Ge^\bullet + {}^\bullet O–Si\equiv \tag{6}$$

$$\frac{dN'_R}{d\tau} = -N'_R e^{-E_G/kT} + n_a \frac{n'_b}{N_T}.$$

Reaction 7

$$\equiv Si–O^\bullet + {}^\bullet O–Si\equiv \leftrightarrow \equiv Si–O–O–Si\equiv \tag{7}$$

$$\frac{dN_A}{d\tau} = -N_A e^{-E_A/kT} + n_a \frac{n_a}{N_T}.$$