Simulation of Porous SiO_x Layer Growth

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ABSTRACT

Monte Carlo simulation of deposition of amorphous SiO_x layer on a polymer surface is reported. The model developed is based on the network properties of silica and takes into account dangling bonds arising during the real process of deposition. Porosity of the simulated amorphous layer is characterized by the porous relative volume and relation of the porous surface to their volume. The results are presented for different nucleation sites densities (NSD) on the polymer surface and for various energies of arriving Si and O atoms. We found the porosity decreases as the NSD increases. At low NSD values $\lesssim 1$ site/nm^2 porosity can be remarkably decreased by an increase of the energy of deposited particles.

Keywords: *Monte Carlo simulation, amorphous silica, porosity, radial distribution function, bond angle distribution function.*

1 MODEL

Thin amorphous layers are widely used for improvement of gas barrier properties of polymer films in electronic and packaging industries. The barrier properties of the layers are driven by their structural properties. It is therefore worth modelling these properties using atomistic modelling.

Modelling of the amorphous layer growth can be made within Keating-like valence force model [1], which has been successfully employed recently for description of amorphous systems like silica [2]. These studies were performed using Monte Carlo (MC) simulation within continuous random network (CRN) model treating definite number of atoms and bonds. The principal event in this model which pulls the system over its phase space consists in pair bond switching: randomly chosen bonds AB and CD (A, B, C, and D denote particular atoms) are changed to form new bonds AC and BD and no dangling bonds is allowed.

In real growth process the dangling bonds are inevitable, therefore to simulate the growth one has to go beyond the CRN model by taking into account the dangling bonds and consequently modifying the phase space exploring mechanism. The latter in contrast to the pair bond switching event consists in separate bond breaking (creation of two dangling bonds) and bond formation (annihilation of two dangling bonds) events. Obviously only stretched bonds can be allowed to be broken. A possibility for a dangling bond to jump from an atom to its fully coordinated neighbor is also taken into account. To make bonding favourable certain energies $E^d_{\rm O}$ =4 eV and $E^d_{\rm Si}$ =1 eV have been ascribed to dangling bonds of oxygen and silicon respectively. Thus, the energy of the growing layer related to topology of the system is determined as

$$E_{top} = \tfrac{1}{2}\sum_{i,j} K^r_{\alpha\beta}\cdot\left(r^{\alpha\beta}_{ij}-r^{\alpha\beta}_0\right)^2 + \tfrac{1}{2}\sum_{n,m} K^\theta_{\alpha\beta\gamma}\times \left(\cos\theta^{\alpha\beta\gamma}_{nm}-\cos\theta^{\alpha\beta\gamma}_0\right)^2 + N^d_{\rm Si}\cdot E^d_{\rm Si} + N^d_O\cdot E^d_O, \quad (1)$$

where α,β,γ = Si or O, $N^d_{\rm Si}$ and N^d_O are numbers of the dangling bonds of Si and O respectively. Values for the nearest neighbor force constants $K^r_{\alpha\beta}$ and $K^\theta_{\alpha\beta\gamma}$, bond lengths $r^{\alpha\beta}_0$ and bond angles $\theta^{\alpha\beta\gamma}_0$ used in the simulations are given in the Table. Structure of the growing layer is driven by diffusion of dangling bonds and their annihilation. In fact, the diffusion of dangling bonds results in atomic diffusion. An additional repulsive force

$$F^{\alpha\beta}_{ij} = K\cdot(r^{\alpha\beta}_{ij}-r_1) \quad \begin{cases} r^{\alpha\beta}_{ij} < r_1, \\ 0 \quad otherwise \end{cases} \quad (2)$$

with K =0.13 eV/Å^2, r_1 =2.7 Å was introduced between nearest unbound atoms α and β to ensure correct average density of the material $\rho \lesssim$2.2 g/cm^3.

An active (nucleation) site of a polymer could arise due to breaking of some bond in a polymer molecule on its surface. For polyethylene terephthalate (PET) this can be C=O bond, so it seems reasonable to consider an oxygen dangling bond as a nucleation site in PET. As the polymer surface is only partly crystalline the nucleation sites were supposed to be randomly distributed over the surface and firmly attached to it. The polymer surface for simplicity was considered ideally flat. Topology of the surface maybe important and will be implemented in future calculations. We neglect O-O bonding

$K^r_{\text{Si-O}}$	27.0 eV/Å^2
$K^r_{\text{Si-Si}}$	9.08 eV/Å^2
$K^\theta_{\text{Si-Si-Si}}$	3.58 eV
$K^\theta_{\text{Si-Si-O}}$	3.93 eV
$K^\theta_{\text{O-Si-O}}$	4.32 eV
$K^\theta_{\text{Si-O-Si}}$	0.75-2.0 eV
$r_0^{\text{Si-O}}$	1.6 Å
$r_0^{\text{Si-Si}}$	2.35 Å
$\cos\theta_0^{\text{Si-O-Si}}$	-1
$\cos\theta_0^{\text{O-Si-O}}$	-1/3
$\cos\theta_0^{\text{Si-Si-Si}}$	-1/3
$\cos\theta_0^{\text{Si-Si-O}}$	-1/3

Table 1: Model parameters

in our model and therefore Si atom is put on top of every nucleation site from the very beginning.

Simulation was performed in a box with cross section 30×30 Å^2 using cyclic boundary conditions within xy plane and was restricted by deposition of 6000 Si and O atoms with average ratio 1:1.8 (x =1.8). Simulated growth consists in two sequential and repetitive stages: i) particle arrival into the system; ii) equilibration of the system via MC simulation of dangling bond creation, diffusion and annihilation. According to the average composition silicon or oxygen atom is chosen and delivered at random to a dangling bond located in a surface layer 3-15 Å thick. The layer thickness naturally depends on an average kinetic energy of the particle. After delivery of every four particles the system is equilibrated over up to 1500 MC moves depending on the number of dangling and stretched bonds. Each MC move is accepted or rejected according to Metropolis scheme on a basis of E_{top} and an effective temperature. The temperature in the vicinity of four recently arrived particles is taken to be higher (by 0.5 eV or 1.0 eV) than that of the rest of the system (0.05 eV), to take into account the kinetic energy of the arriving particles.

2 RESULTS

2.1 Radial Distribution Function

Typical radial distribution function (RDF) and bond angle distribution functions (BADF) for the simulated structures are shown in Figs 1 and 2 respectively. According to Fig.1 only short range correlations ($r \lesssim 5$ Å) are observed which is consistent with the RDF obtained by molecular dynamics simulations for bulk SiO_2 glass densities higher than 1.6 g/cm^3 [3]. The Si-O and Si-Si bond length peaks (labelled 1 and 2 respectively) are well pronounced. The position of peak 1 and its full width at half maximum (FWHM) are very close to those in bulk glass SiO_2. In contrast, the second neighbor O-O and Si-Si peaks and the third neighbor Si-O peak (labelled 3, 4, and 5 respectively) are noticeably broader and much less pronounced than those in bulk glass [4]. This might be explained by influence of the bond angles variation reflected in the BADF.

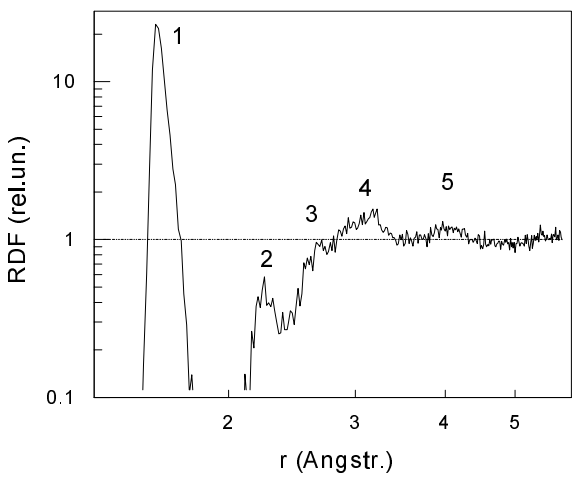

Figure 1: Typical shape of the radial distribution function (RDF) for the simulated SiO_x structures (see text). Peaks correspond to: 1) nearest neighboring Si for O and vice versa; 2) nearest neighboring Si for Si; 3) second neighboring O for O; 4) second neighboring Si for Si; 5) third neighboring Si for O and vice versa.

2.2 Bond Angle Distribution Functions

Bond angle distribution functions are quite broad especially that for the Si-O-Si bond angle (Fig.2). The O-Si-O bond angle distribution (solid line) peaks at the equilibrium angle $\sim$109^o with FWHM about 25^o. The latter is 2.5 times higher than the experimental value for bulk SiO_2 glass [5]. The Si-O-Si bond angle distribution shown by dotted line in Fig.2 possesses a maximum at about $\theta \simeq$130-140^o rather than at the equilibrium angle $\theta \simeq$180^o and is again about 3 times broader than that determined experimentally [6]; the corresponding experimental value of the equilibrium $\theta^{\text{Si-O-Si}}$ for bulk silica is 142^o. The observed properties of the BADF give the evidences either for a substantial distortion of the six-fold rings in the network structure of silica or, more likely, for an existence of other rings, i.e. 3-, 4-, 5-fold ets. rings [4].

RDF and BADF are very little dependent on NSD, particle energy and effective temperature in the ranges studied. The most sensitive parameters of the structures simulated at different conditions are related to their porosity. A porous fraction volume V_{por} and a relation of the porous surface to the porous volume S_{por}/V_{por} were calculated. Corresponding data averaged over several statistically independent structure realizations are

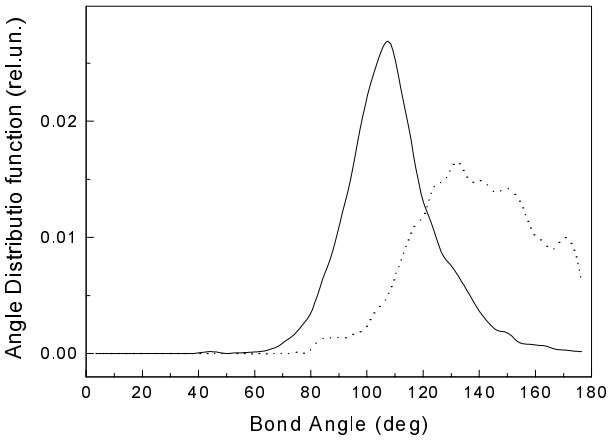

Figure 2: Bond angle distribution functions for O-Si-O and Si-Si-O (solid line) bonds, for Si-O-Si bond (dotted line).

summarized in Fig.3.

2.3 Porosity

Fig.3 shows that there is a tendency for V_{por} to decrease and for S_{por}/V_{por} to increase with the increase of the NSD in the range of NSD $\lesssim$10 nm^{-2} and some saturation at higher NSD values. In the other words, porosity decreases with increase of NSD within the range specified and this may result in a better gas barrier properties of the glass layer. To understand this better a percolation through the simulated porous structures will be studied.

The calculated porosity parameters in Fig.3 are basically concentrated around dashed curves. Worth to note that even a change in $K^{\theta}_{\mathrm{Si\text{-}O\text{-}Si}}$ does not affect very much these dependences as much as the particle energy and the substrate temperature do. One can find a tendency to a better structure properties if the layer is grown using higher (1.0 eV) kinetic energy for the deposited particles; this effect is more pronounced at low NSD values. This result is qualitatively consistent with the fact that sputtered silica films on a PET substrate are often thought to possess better structure properties than those obtained by electron beam deposition technique.

3 SUMMARY

We performed Monte Carlo simulation of deposition of amorphous SiO_x layer on a polymer surface as a function of nucleation site density and temperature, effectively taking into account the kinetic energy of the arriving oxygen and silicon atoms. We found that porosity decreases with increase of NSD until it reaches 10 nm^{-2} after what only minor changes are observed. At

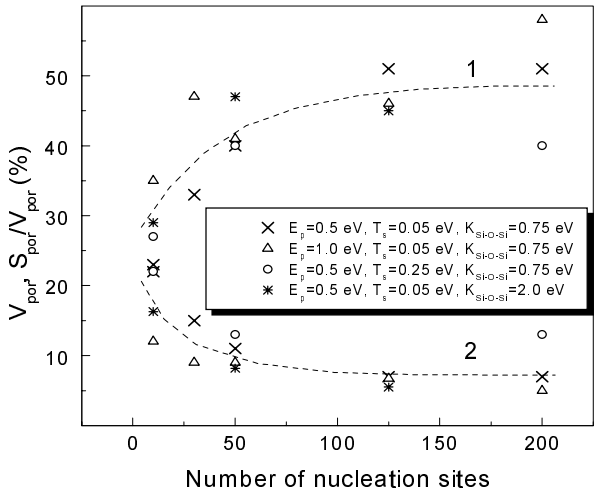

Figure 3: Porosity as a function of nucleation cite number for different particle energy E_p, substrate temperature T_s and Si-O-Si bond bending force constant K. Symbols correspond to calculated data from simulated structures, curves are guide to the eye: 1) pore surface-to-volume ratio, 2) relative pore volume.

low NSD values $\sim$ 1 nm^{-2} porosity can be remarkably decreased by an increase of the energy of deposited particles.

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