Multicomponent Glass Surfaces:
Structure and Adsorption

Progress Report

Stephen H. Garofalini

Department of Ceramics
Rutgers University
Piscataway, NJ 08855

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The intent of the research is to study the composition and surface structure of complex multicomponent silicate glasses and the effect that these surfaces have on adsorption behavior, thin film formation, and adhesion. Classical molecular dynamics (MD) simulations, quantum molecular dynamics simulations using the Car-Parrinello (CP) MD technique, and XPS and UHV-AFM Force-Distance (FD) experiments are being used in this program.

I. CLASSICAL SIMULATIONS:

Employing an accurate algorithm for classical simulations of the adsorption of EAM model Pt metal adatoms from the gaseous state onto silicate surfaces showed adsorption behavior similar to that for adsorption of Lennard-Jones (LJ) Pt adatoms. That is, the adatoms adsorb and penetrate the substrate similarly and alter the glass surface similarly. The alteration of the glass surface can have important implications on the reactivity of the surface and we have initiated analysis of this.

In an extension of the interactions between a model LJ Pt metal vapor and the silica glass surface, we are studying the interaction of crystalline LJ Pt metal in contact with the glass surface. Two aspects are being covered: (1) the effect of elevated temperature on the interdiffusion at the interface for the two phases in 'contact', and (2) the effect of room temperature compression and withdrawal on structural changes in the glass. The former relates to maximizing bonding between crystal and glassy phases, as used in composites; the latter relates to polishing and grinding processes, as well as composite interfaces after imposition of stress.

In order to determine what is meant by 'contact' in part (1) due to the atomistically rough topography of the glass surface, the crystal was slowly moved towards the glass surface while the force normal to the surface was monitored. Results showed the attractive and repulsive regions similar to an FD curve of the AFM type, but with shorter range and greater detail. By placing the crystal at the equilibrium (zero stress) distance from the glass surface and heating, the diffusivities of the surface atoms in the crystal were much higher than those observed when the crystal is in contact with a vacuum. This indicates the significant role of the open network glass phase in contact with the crystal in lowering temperatures for sintering between the two phases. When the separation distance between the two phases was at the maximum in the attractive stress, $\sim 2-3 \text{ \AA}$ larger separation than at zero stress, the crystal atoms diffused into the glass as before, but there was a decrease in the diffusion of the glass atoms into the crystal phase. This indicates a lowering of intermixing and potential weak bonding points at crystal/glass interfaces which have small (few $\text{\AA}$) roughness. In part (2), there is an effect of the compression and withdrawal of the crystal on the glass surface structure, creating a memory of the compression. A large decrease in the Si-O-Si bond angle distribution occurs and there is an increase in the number of 3-membered rings. Since smaller bond angles and 3-membered rings are more reactive than larger bond angles and rings, the simulation result has important implications on the reactivity of glasses which are subjected to interactions with condensed phases (polishing, crushing of glasses, composites, etc.). Additional discussion of this is presented in the proposed research for the coming year. In addition, the work in part (2) has shown the role of non-bridging oxygens, NBO, on the maximum attractive strength

upon withdrawal of the crystal (called the adhesive strength in AFM-FD terminology).

Whereas some of our previous work involved adsorption of strongly interacting, and heavy, model Pt gas adatoms, we recently finished a study of adsorption of weakly interacting inert gas molecules/atoms (N_2 , Ar, and Ne) onto silica, sodium aluminosilicate, and in the Ne case, sodium silicate glasses. While Pt adsorbs $\sim 6\text{\AA}$ on these surfaces, the larger, weak inert gases N_2 and Ar, do not show penetration. Ne, however, shows some penetration into silica, but none on the surfaces which contain the sodium ions. This indicates the role of the Na ions on decreasing the atomistic roughness of the glass surface and limiting the number of sites to which the adatoms can adsorb/absorb.

II. QUANTUM CALCULATIONS:

We have used the CP technique and density functional theory within the local density approximation and ultra-soft pseudopotentials to study the crystalline forms of silica prior to using the technique to study amorphous silica and silica surfaces. The latter two are computationally more difficult to study than the crystalline systems because of system size, even with the use of ultra-soft pseudopotentials. Recently, we performed energy minimization with this technique to determine low energy structures, density of states, and equation of state data for the crystals. In our simulations of the crystalline forms, we have been able to use an IBM RISC 6000 workstation with efficient turn-around time rather than having to rely on a supercomputer. This attests to the usefulness of the CP algorithm which we use and our application of ultra-soft pseudopotentials. We have also successfully completed a study of the sodium metasilicate crystal with this technique, thus introducing alkali ions into the calculations. In addition, we are completing calculation of the structure of a silica surface.

III. UHV-AFM EXPERIMENTS:

On the experimental side, we have generated FD curves in our UHV-AFM to measure adhesive forces between a tip and different silicate glasses and nanoheterogeneity which might exist on these surfaces. Recently, we have used FD microscopy to test an idea: could we determine the different reactivities between dissimilar materials rather than having to resort to sessile drop tests, pull tests, etc. To test this, we used the elements in brazing metals and Si_3N_4 . It is known that Ti is the reactive metal in Ti-Cu-Ag brazing alloy used to bond metals to Si_3N_4 . By bringing a silicon nitride tip in contact with foils of each individual metal, we were able to show that the Ti interacted much more strongly than the other two, as seen in its FD curve. This indicates a possibility of using AFM-FD to scan potential coating/substrate materials of interest. This should help us determine the bonding heterogeneity that may exist in coating/substrate systems. An example of this would be the interaction between a catalyst metal support washcoat species, such as titania, with a substrate such as a steel or cordierite, as used in automotive catalysts.

MOST RECENT PUBLICATIONS SUPPORTED BY THIS GRANT:

"Structural and Electronic Properties of Sodium Metasilicate", F. Liu, S. H. Garofalini, R.D. King-Smith, and D. Vanderbilt, Chem. Phys. Lett. (accepted).

"A First Principles Study of Crystalline Silica", F. Liu, S. H. Garofalini, R.D. King-Smith, and D. Vanderbilt, Phys. Rev. B (submitted).

"Distribution of Non-Bridging Oxygens in Vitreous Silica Surfaces", F. Liu and S. H. Garofalini, J. Non-Cryst. Sol. (submitted).

"Surface Distribution of Ions and Adsorption Behavior of Calcium Disilicate Glasses", S. H. Garofalini, J. Non-Cryst. Sol. (submitted).

"First Principles Calculations of the Structural Properties of β -Cristobalite", F. Liu, S. H. Garofalini, R.D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. 70 (1993) 2750.

"AFM and XPS Investigation of the Onset of Reactions on Alkali Silicate Surfaces", G. Rudd, S. H. Garofalini, D. A. Hensley, and C. M. Mate, J. Am. Cer. Soc. 76 (1993) 2555.

"Deposition of EAM Pt on Silicate Glass Surfaces", E. Webb and S. H. Garofalini (to be submitted).

"Adsorption of Inert Gas Atoms onto Silica and Silicate Glass Surfaces", A. Kohler and S. H. Garofalini, (to be submitted).

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