

## Communication: An obligatory glass surface

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## Communication: An obligatory glass surface

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Theory predicts, and experiments have shown, that dynamics is faster at glass surfaces than in the bulk, allowing the glass to settle into deeper energy landscape minima, or “age more.” Is it possible that a glass surface could survive at temperatures where the bulk crystallizes, or that it could remain glassy after the bulk is heated all the way to its melting temperature and re-cooled? We image in real-time and with sub-nanometer resolution the two-state surface dynamics on a cerium-based glass surface, from deep within the glassy regime to above the crystallization temperature. Unlike other surfaces that we have studied, this glass surface remains amorphous even after the bulk re-crystallizes. The surface retains non-crystalline structure and two state dynamics of cooperatively rearranging regions even after heat annealing to just below the bulk melting temperature. The heat-annealed cooperatively rearranging regions are larger than originally, a sign that the surface is well aged. The surface dynamics depends weakly on temperature, showing no sign of the superexponential increase in bulk dynamics expected near  $T_g$ . © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757975>]

When a liquid is supercooled, the length scale of its cooperative atomic motions increases, eventually “freezing in” at  $\approx 5$  atomic diameters near the bulk glass transition temperature.<sup>1</sup> On the surface, the length scale of cooperatively rearranging regions (CRRs) is predicted to be similar, with about half the barrier for relaxation.<sup>2</sup> Larger cooperative regions are unlikely to form because the decreasing mobility in the supercooled liquid overwhelms the increasing length scale of cooperativity when the temperature is lowered.

Glass surfaces are beginning to play an important role in our understanding of the glass transition. We have just begun to appreciate the differences between the bulk glass and its surface.<sup>3–6</sup> Glass surfaces possess many orders of magnitude enhanced mobility relative to the bulk.<sup>5,7–10</sup> As a result, glass surfaces can relax much deeper on the energy landscape than is possible for the bulk on reasonable time scales.<sup>11</sup> In addition, the surface mobility increases more slowly with temperature than in the bulk, both for individual cooperatively rearranging regions,<sup>12</sup> and on average.<sup>5</sup> Could the weak temperature dependence of surface mobility result in a glass surface that is highly robust, persisting even when the bulk is heated above its crystallization temperature and to its melting temperature?

It turns out that a metallic glass with such a surface does exist, even though metallic glass surfaces normally crystallize at temperatures below the bulk.<sup>13</sup> We studied the cerium-based glass  $\text{Ce}_{62}\text{Al}_{10}\text{Cu}_{20}\text{Ni}_5\text{Co}_5$  with an ultra-low bulk glass transition temperature. The low glass transition temperature allowed us to image the hopping dynamics of cooperatively rearranging regions by scanning tunneling microscopy (STM), from deep within the glassy regime to above its bulk crystallization temperature  $T_x$ . The surface remains

amorphous above  $T_x$ , whereas calorimetry shows that the bulk becomes crystalline. The surface is still glassy after the sample is annealed at its melting temperature and cooled back to room temperature, based on both STM imaging and x-ray diffraction. The CRRs of the heat-annealed glass increase in size, consistent with a well-aged glass surface. We observe only a weak dependence of surface dynamics on temperature. We propose several causes for this observation: compensation between thermal activation and increased barrier height of larger CRRs upon annealing; a higher  $T_g$  for the surface than the bulk; and a broad distribution of rates that is sampled by our limited experimental dynamic range.

Glass samples were prepared by arc melting the pure elements in a Ti-gettered Ar atmosphere.<sup>14</sup> The purity of Ce was about 99.5 mass % and the other elements had a purity of at least 99.99 mass %. The alloy ingots were remelted and suck-cast into a Cu mold to get the desired shape. Figure 1 illustrates the bulk thermal and structural properties of the Ce glass. The differential scanning calorimetry in Fig. 1(a) was obtained on a Mettler Toledo DSC 821. The bulk glass transition temperature lies at  $T_g \approx 377$  K, marked by a characteristic step in the heat flow as observed previously for similar glasses.<sup>14</sup> Bulk crystallization occurs as an exothermic event at  $T_x \approx 433$  K. The sample begins to melt at  $T_m \approx 626$  K, yielding solids and liquids of different composition. At the liquidus point  $T_L \approx 647$  K, no solid remains. When a sample heated  $10^\circ$  above the bulk  $T_x$  is analyzed, no trace of the glass transition or crystallization remains (red trace in Fig. 1(a)). Figure 1(b) illustrates what happens structurally, using x-ray diffraction on a Siemens Bruker D5000 (Cu  $K\alpha$  radiation): the cast glass sample has only a diffuse peak at  $2\theta = 32^\circ$ , characteristic of amorphous structure.<sup>14</sup> When the sample is heated

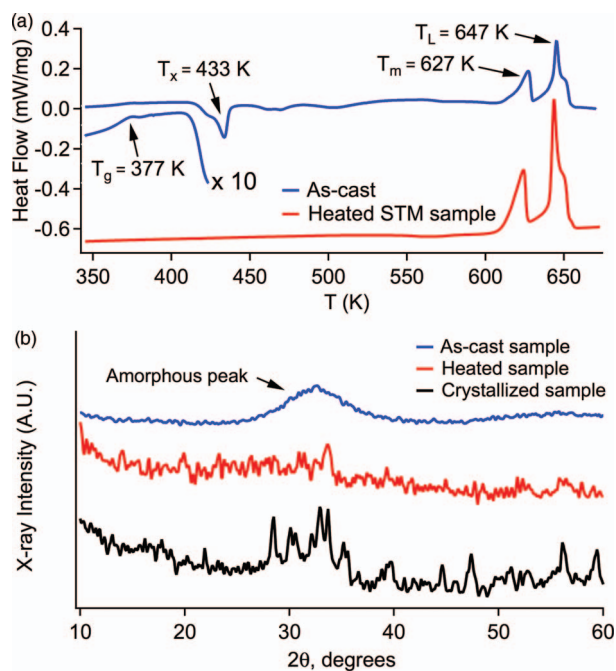


FIG. 1. Calorimetric and structural properties of the bulk Ce glass. (a) The blue trace shows the differential scanning calorimetry (DSC) of the Ce glass as-made. The glass transition step occurs at  $T_g \approx 377$  K, the crystallization peak (exothermic) at  $T_x = 433$  K, the melting peak (endothermic) at  $T_m \approx 627$  K, and the liquidus peak (where no solid of any composition remains in equilibrium with the liquid) at  $T_L \approx 647$  K. The red trace shows DSC of a sample that was scanned in the STM at 295 K, then heated in the STM to 443 K  $> T_x$  and scanned there. The  $T_g$  step and  $T_x$  peak are completely absent, indicating bulk crystallization. The melting and liquidus peaks remain. The red trace is shifted along the Y-axis for clarity. (b) X-ray diffraction intensity vs. scattering angle  $2\theta$  for Ce glass samples annealed to three temperatures. As-cast Ce glass (blue) has the broad amorphous peak at  $32^\circ$ . When heated near melting point in the STM (to  $\approx 627$  K), the amorphous peak disappears (red trace). Complete melting at 673 K for 20 min ensured complete bulk crystallization, revealing multiple crystalline peaks (black trace).

below the bulk melting point, this diffuse peak disappears and sharper diffraction peaks begin to appear. Heating to the liquidus momentarily and recooling the sample results in sharp diffraction peaks characteristic of a crystalline sample.

To prepare surfaces for STM imaging, samples were first degassed at 336 K for 10 h. Next, native oxides were removed by one of two methods: abrasion or ion sputtering. Sample surfaces were abraded with a stainless steel blade *in situ* in the UHV-STM chamber to avoid any change from the bulk composition. The silvery abraded surface is visually very distinct from the yellow oxide surface. Ion sputtering was performed using 2 keV argon ions, in a load chamber backfilled with high-purity argon to  $2 \times 10^{-3}$  Pa (background pressure  $< 6 \times 10^{-6}$  Pa). About ten 25-min cycles of sputter-cool-sputter were performed to keep the sample temperature well below  $T_g$ . X-ray photoelectron spectroscopy with a Physical Electronics PHI5400 diffractometer ascertained that sputtering enriches the surface composition in cerium, to  $\text{Ce}_{84.6}\text{Al}_{4.2}\text{Cu}_{9.81}\text{Ni}_{1.47}\text{Co}_0$ . As shown by Wang and co-workers, this composition still lies within the glassy range of the alloy.<sup>14</sup> The abraded and sputtered surfaces had the same surface morphology when scanned by STM, and yielded the same kinetics within measurement uncertainty. The dynamics observed is thus independent of surface preparation, at least

for these two surfaces. Since the abraded surface is exposed bulk sample, this observation supports the notion that surface glass dynamics can be approximated by bulk glass dynamics with a reduced barrier to account for higher mobility.<sup>2</sup>

Our UHV-STM was equipped with a custom-built sample heater, whose 4 W resistive coil is driven by a 0–30 V power supply. Successive STM images were acquired at 1–2 min time intervals to obtain movies of surface dynamics at temperatures ranging from 295 K up to 443 K. *In situ* temperature measurements are provided by a thermocouple mounted next to the STM sample. To heat samples to the melting point, they were cycled into an adjacent UHV preparation chamber and resistively heated (20 A, 2.5 V) for 2 min, until surface buckling was observed at  $T \approx 627$  K.

What does the dynamics of the surface look like at different temperatures? Typical two-state hopping dynamics of atomic clusters is illustrated in Fig. 2 on both sputtered and abraded glass surfaces (see also movie in the supplementary material<sup>15</sup>). Figures 2(a) and 2(b) show two-state dynamics of CRRs at room temperature. All mobile clusters were compact in shape and had characteristics (heterogeneous hopping dynamics, size distribution 0.5–2 nm averaging 4 atomic diameters) similar to those previously observed for metallic glass surfaces and amorphous silicon.<sup>5,9</sup> This further corroborates

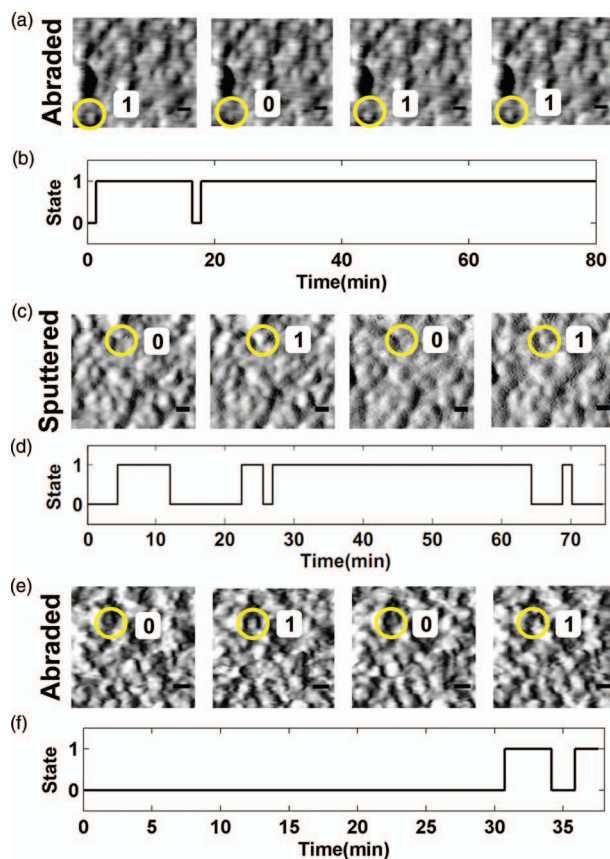


FIG. 2. Two-state dynamics on cerium glass surfaces. (a) Four frames from a STM movie of an abraded surface at 295 K, with the encircled CRR exhibiting two-state motion. (b) Its full time trace. (c) and (d) Similar two-state dynamics on an ion-sputtered surface at 376 K (see also movie in the supplementary material).<sup>15</sup> (e) and (f) Similar dynamics on an abraded surface at 443 K. The scale bar equals 2 nm. The sampling rate for the movies was about 1.5 min/frame.

our claim<sup>9</sup> that the CRRs on glass surfaces share a universal size distribution, and exhibit both spatially (CRR-to-CRR rate variations) and temporally (rate variations within a single cluster trace) heterogeneous kinetics. Figures 2(c) and 2(d) show what happens when the surface is imaged at 376 K, right at the bulk glass transition: Similar two-state dynamics continues on the surface unperturbed. Even at 433 K (Figs. 1(e) and 1(f)), 10° above the bulk crystallization temperature, the surface shows no sign of crystallization after extensive search by STM imaging, and surface CRRs continue to hop between two states. The glass surface thus remains robust at temperatures where the bulk has become crystallized (Fig. 1). Large-scale lateral motion or diffusion was not observed up to 433 K. We previously observed lateral three-state motion in other metallic glasses,<sup>5</sup> so we expect that such motions could occur on the Ce glass surface above 433 K.

To what extreme can the bulk and surface be uncoupled for our Ce glass? We annealed the surface just below the bulk melting temperature in UHV (2 min at 627 K). After very slow cooling back to room temperature, we searched the surface extensively (20 different areas) for signs of crystallinity by STM. We had detected such crystallinity previously upon annealing other surface glasses.<sup>9</sup> Instead we found that the Ce glass CRRs had grown in size by a factor of 1.5 (compare Figs. 3(a) and 3(b), see arrow in Fig. 4(b)). The large CRRs have an average diameter of 6 Ce atoms, and represent a very well-aged glass surface. The large clusters still hop (Fig. 3(c)), but at a lower rate than the original CRRs (Fig. 4(a) open vs. closed circle at 295 K).

These results can be compared with our previous imaging results as well as prior studies in the literature. We recently reported both ensemble averaged and individual CRR hopping rates for different glasses as a function of temperature below  $T_g$ . The average rate (number of CRRs hopping per nm<sup>2</sup> per minute) could be fitted to an Arrhenius plot with an activa-

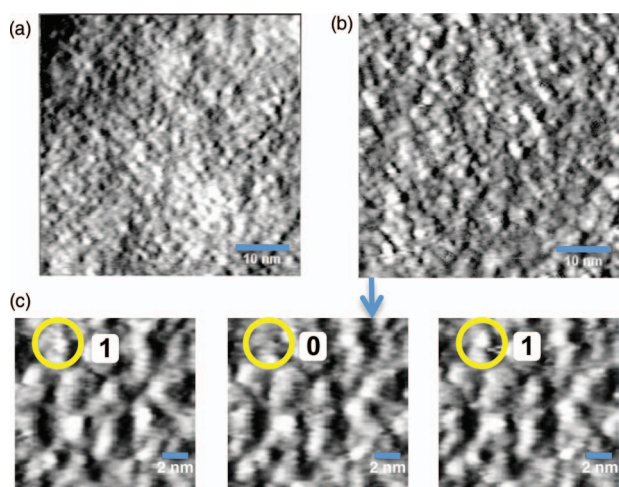


FIG. 3. Robustness of glass surfaces and large CRR size after annealing near the melting temperature. (a) The cluster size of an abraded amorphous surface imaged at 295 K. (b) The sample after heating near ( $\approx 627$  K) the bulk melting temperature, and cooled back to room temperature. Cluster size has increased by a factor of  $1.5 \pm 0.05$  (based on the ratio of widths of spatial autocorrelation functions for (a) and (b)). (c) Three frames from a movie of the annealed surface in (b) at room temperature: the larger CRRs still undergo two-state hopping.

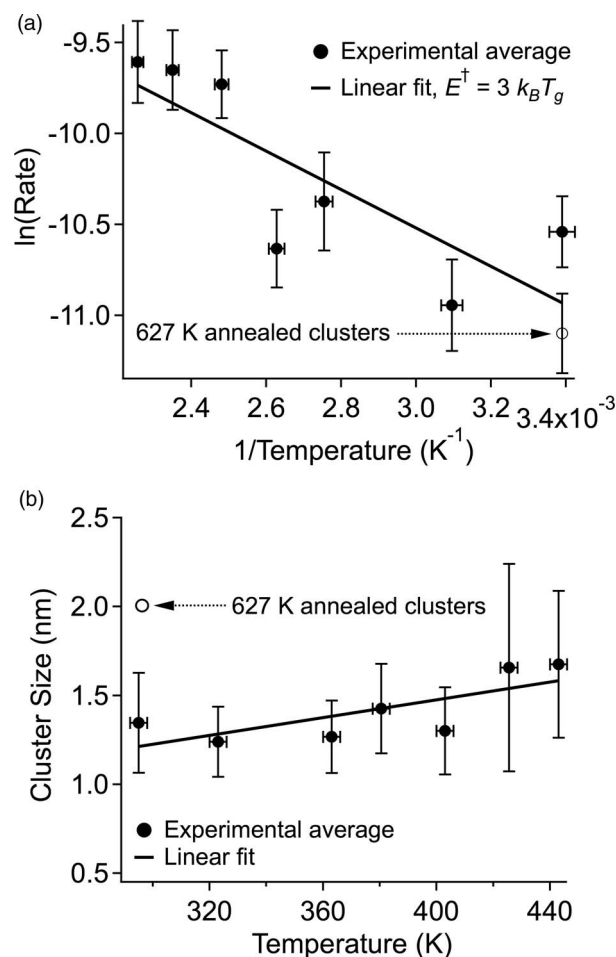


FIG. 4. Temperature dependence of the number of CRRs hopping, and of CRR size. (a) The temperature dependence of the average CRR hopping rate ( $\text{nm}^{-2} \text{min}^{-1}$ ) as an Arrhenius plot. Data for the average over all sputtered and abraded surfaces are shown. Error bars were calculated based either on the scatter of repeated measurements at a given temperature ( $1\sigma$ ), or by assuming Poisson statistics when there is only one measurement for a given temperature. (b) The average size and standard deviation of size of mobile CRRs with temperature. At most a weak increasing trend of atomic cluster size with temperature was observed, from 1.25 to 1.5 nm. A much larger increase to 2 nm is observed when the surface is annealed to  $\approx 627$  K, then imaged at room temperature: the arrow and open circle show the data for the surface in Figure 3.

tion barrier of  $\approx 3 k_B T_g$ .<sup>5</sup> Hopping rates of individual clusters monitored as a function of temperature required an activation energy of  $\approx 10 k_B T_g$ .<sup>12</sup> We suggested that the limited dynamic range of our experiments is responsible for the difference: some CRRs get too fast to be sampled by our STM movies, and formerly immobile CRRs enter our dynamic range upon heating, keeping the ensemble-averaged rate nearly constant.<sup>5</sup> Rate measurements on many individual CRRs support a wide (power law) rate distribution.<sup>12</sup>

On the Ce glass surface, individual CRRs also hop more frequently when heated, although we did not obtain enough statistics for a quantitative fit. Figure 4(a) shows an Arrhenius plot of the ensemble averaged rate (events per nm<sup>2</sup> per minute), extending from well below the bulk  $T_g$  to well above the bulk  $T_x$ . The rate depends only weakly on temperature, with the effective activation energy of  $\approx 3 k_B T_g$  ( $\approx 9$  kJ/mol) from the slope of the Arrhenius plot. This

value is in line with the ensemble-averaged rate obtained for other metallic glass surfaces,<sup>5</sup> and the limited dynamic range explanation still applies.

Limited dynamic range alone cannot explain why hopping continues past the bulk  $T_g$  and  $T_x$ . Over that wide temperature range, the bulk dynamics usually speeds up by 10 orders of magnitude (30–40  $k_B T_g$  bulk barrier), based on relaxation peak observations for many glass-formers, including polymers, inorganic, organic, and even metallic glasses.<sup>16–18</sup> A surface-bulk crossover occurs in polymers just above  $T_g$ ,<sup>7,19</sup> and our results indicate it must be even higher for the Ce-based glass. In addition to dynamic range, we suggest two more rationales for the weak temperature dependence of the surface hopping rate. Figures 3(a), 3(b), and 4(b) show that the average diameter of mobile CRRs increases by about a factor of 1.5 upon annealing near the bulk melting temperature. (A weak trend may also exist between 310 and 440 K in Fig. 4(b), but the uncertainty in the size distribution is too large to say with confidence.) Random first order theory predicts that activation barriers depend inversely on the size of CRRs,<sup>20</sup> so larger annealed clusters should hop more slowly. This rationale states that thermal activation is offset by a higher barrier as the temperature increases. The second rationale is that the surface glass transition temperature could be higher than in the bulk, so rapid surface diffusion does not start until well above  $T_x$ . Figure 2 illustrates that the surface morphology undergoes no significant change from well below  $T_g$  to above  $T_x$ , and we did not see three-state hopping or larger lateral motions even above  $T_x$ . This behavior differs from other metallic glass surfaces<sup>5,13</sup> as well as amorphous silicon:<sup>9</sup> surface crystallization is easily detected when the sample is annealed at higher temperatures.

Faster dynamics and better aging have been observed previously for other types of glass surfaces. Ediger and co-workers observed that the mobile surface layer of a molecular glass created by vapor-deposition corresponded to an aged bulk glass cooled slowly for 1000 years.<sup>11</sup> The aging of our CRRs by annealing from below  $T_g$  is in contrast to supercooling a liquid from above  $T_g$ . In the former case annealing increases the cooperative length scale, in the latter case a longer cooling process allows growth of the cooperative length scale. Berthier and co-workers<sup>1</sup> measured a length scale growing from 0.9 nm to 1.5 nm while cooling ever further below  $T_g$ . Thus, cluster size is indeed an indicator of how well a glass has aged. A weak temperature dependence for glassy surface dynamics has also been observed by Forrest *et al.*, to the point where they called the dynamics “athermal.”<sup>21</sup>

The Ce glass surface clearly has a number of interesting characteristics. It will cover the crystalline bulk even above the bulk glass transition and crystallization temperatures. It either persists or at least re-forms on samples that were nearly melted. Its CRRs undergo fast two-state hopping. The aver-

age hopping rate has a weak temperature dependence, due to a combination of limited experimental dynamic range, increasing barrier height with temperature, and/or a large difference between the bulk and surface glass transition temperatures. The CRRs on the surface grow in size when the glass is heated from below  $T_g$  to near its melting point, indicating aging of the glass surface. Bulk Ce glasses have very low critical cooling rates (<100 K/s).<sup>1</sup> This implies that the “confusion principle”<sup>22</sup> makes it difficult for the surface atoms to find the crystalline state before they get trapped in a deep local minima in the potential energy landscape. It appears that surface mobility is insufficient to overcome the “confusion,” but enough to produce a well-aged glass with larger CRRs upon annealing.

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<sup>15</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4757975> for STM movie of Ce glass surface dynamics.

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