Direct Imaging of Two-State Dynamics on the Amorphous Silicon Surface

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Amorphous silicon is an important material, amidst a debate whether or not it is a glass. We produce amorphous Si surfaces by ion bombardment and vapor growth, and image discrete Si clusters which hop by two-state dynamics at 295 K. Independent of surface preparation, these clusters have an average diameter of ~5 atoms. Given prior results for metallic glasses, we suggest that this cluster size is a universal feature. The hopping activation free energy of 0.93 ± 0.15 eV is rather small, in agreement with a previously untested surface glass model. Hydrogenation quenches the two-state dynamics, apparently by increasing surface crystallinity.

Amorphous silicon (a-Si) is a low-density solid that can be grown by a variety of processes from ion implantation to chemical vapor deposition (CVD) [1–4]. Unlike conventional glasses, a-Si cannot be produced by rapid cooling of the liquid phase. Thus a-Si is not universally considered a glass, but there is an active debate about the connection between the amorphous solid and liquid phases [5–7].

a-Si shares some characteristics of glasses but lacks others, depending on the method of preparation. Pohl and co-workers observed a plateau in the internal friction of a-Si below 10 K [8]. This plateau is characteristic of glasses, but it disappears when a-Si is passivated with 1% hydrogen [8], indicating that capping by hydrogen settles the bulk into a lower free energy state. The friction plateau and similar behaviors characteristic of glasses well below the glass transition temperature T_g can be rationalized by random energy two-state models [9]. Such models posit that localized two-state dynamics is much more probable than three-state dynamics or diffusion. For example, $1/f$ noise in metallic glasses has been attributed to two-level dynamics of small clusters of atoms [10]. Could such two-state dynamics also persist in a-Si at room temperature? If so, is it still quenched by hydrogenation?

We answer these questions in the affirmative for the a-Si surface: time-lapse movies with a scanning tunneling microscope (STM) directly image small Si clusters hopping between two states at 295 K (Fig. 1). This temperature lies well above the tunneling regime, but also well below the glass transition temperature of a-Si, estimated to be $T_g \approx 900$ K [11]. Visualization of the amorphous surface by STM reveals that compact Si clusters have an average diameter of about 5 Si atoms (Fig. 2). The two-state motion of these compact clusters is direct evidence for the persistence of localized but collective dynamics at a temperature between the glass transition and tunneling regimes. We observed dynamics on a-Si surfaces that have been

amorphized by low energy ion implantation, or vapor grown onto Si substrates. We observe two-state dynamics on both types of hydrogen-free a-Si surfaces (Fig. 1). The dynamics is thus independent of the preparation method. We previously observed two-state dynamics on well-known metallic glass surfaces [12]. There the mobile entities, inferred previously from conductivity measurements [10], also were compact clusters [12].

The time evolution of clusters can be followed for multiple two-state hops, allowing equilibrium constants, rate coefficients, and even changes in rate to be estimated
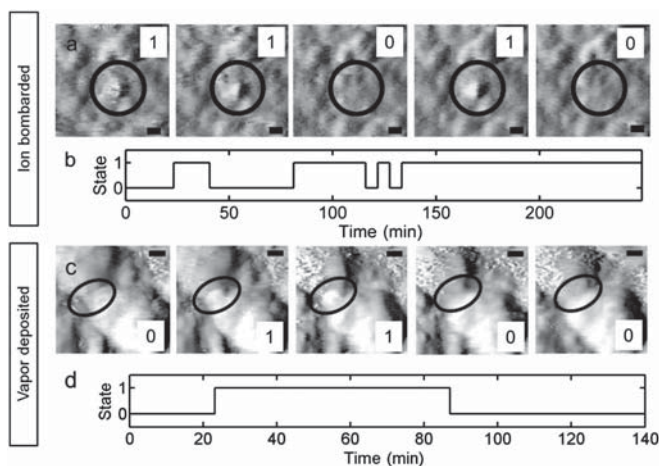

FIG. 1. Two-state dynamics on amorphous silicon surfaces. (a) Five consecutive images on a surface prepared using ion bombardment of a c-Si(100) surface. See movie S1 in the SI [14]. Here, the encircled cluster exhibits a two-state motion while (b) shows the corresponding single cluster trace (SCT) with a time resolution of 6 min. (c) Selected frames from a movie on a-Si surface vapor deposited on a c-Si(100) substrate where the encircled cluster shows two-state dynamics and (d) the corresponding SCT. See movie S2 in the SI [14]. Scale bar is 1.1 nm = 5 at. diam.
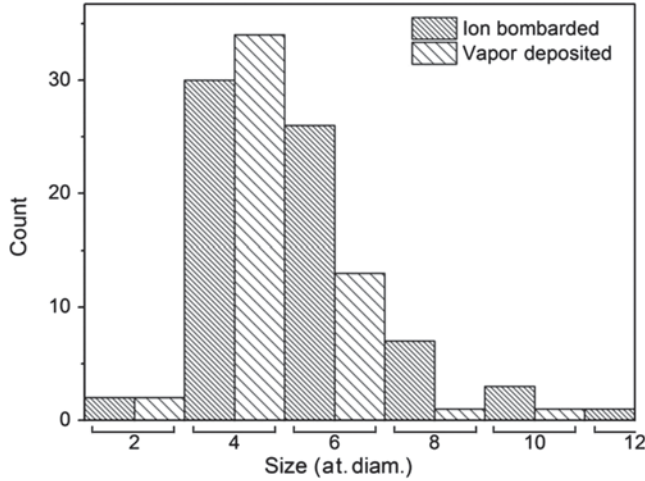
FIG. 2. Cluster size distribution. Histogram showing the cluster size distribution for clusters exhibiting two-state motion (includes all clusters which moved at least once). Each bin is atomic diameters ±1. Both sputtered and vapor-deposited a-Si surfaces are shown.

roughly (Fig. 1). Our temporal dynamic range is about 6–300 min. On these time scales, no diffusive motion of surface clusters is observed at room temperature. At 295 K, <0.5% of the surface clusters hop between two local free energy minima per hour. Some two-state motions occur in concert. Two-state motion ceases almost entirely after the surface is hydrogen passivated.

The silicon samples used in our study were cut from a 0.5 mm thick Si(100) wafer (Montco Silicon Technologies Inc.) that was boron doped to a resistivity of 0.01–0.02 Ω cm and flash heated at 1200 °C to get a 2×1 reconstructed surface. Two surface amorphization methods were used. Some samples were placed in a sputtering chamber connected to the STM. The chamber was backfilled with high-purity argon to 3×10^{-5} torr. An ion gun produced 1.5 keV Ar$^+$ ions at a current density of 1–10 μA/cm^2 for 10–14 h. This dose is at much lower ion energy and has 10–100 times lower flux than that which would produce large Ar voids ("bubbles") in the solid. [Compare Fig. 3 in Ref. [13] with Fig. S1 in the supplemental information (SI) [14].] The subsurface contains mostly very small voids (≤2 nm). The process of flash heating and low-intensity ion bombardment reversibly cycled the surface between crystalline and amorphous. Other samples were prepared by evaporating a 5–10 nm layer of Si atoms onto the crystalline Si(100)-(2×1) reconstructed surface. The evaporation source was the same boron-doped Si(100) wafer used throughout this study. The evaporation was done in a UHV preparation chamber attached to the STM chamber to avoid any surface oxide formation. STM movies of the glass surface were recorded on a homebuilt STM using the design from [15]. The base pressure was below 10^{-10} torr. A bias voltage of -2 V and a tunneling current of 10 pA were employed for

all scans. The STM images presented here are the spatial derivatives of the topographic (variable height-constant current) images. Tip effects on the cluster dynamics were avoided as discussed in the SI [14].

Figure 1 illustrates the movies obtained in our study (see movies S1 and S2 in SI [14]). Si clusters on the surface hop between two structurally distinct states at 295 K. The two-state dynamics involves both vertical and in-plane motion over distances on the order of 1 nm, comparable to the cluster diameter. Altogether, 13 clusters executing two-state hops were observed in different movies on both types of a-Si surfaces. Diffusive motion was not observed.

The average rate derived from single cluster traces (e.g., Figs. 1 and 3) was $k_{obs}(295 \text{ K}) = 0.18 \pm 0.06$ min^{-1} (1 standard deviation). As can be seen in the sample frames of the movie in Fig. 1(a), the hopping occurred between times when the tip scanned over the cluster. Therefore the rates reported here are lower limits. Assuming an Arrhenius law, the observed rate coefficient (sum of forward and backward rate coefficients) is given by

$$k_{obs}(T) = k_0 e^{-\Delta G^\dagger/k_B T} 2 \cosh(\Delta G/2k_B T).$$

We obtain an average activation energy of $\Delta G^\dagger = 0.93 \pm 0.15$ eV ($12 \pm 2k_B T_g$ in units of the glass transition temperature ≈ 900 K). In the above equation, $k_0 \approx 3$ ps is the assumed prefactor for barrier-free hopping, and ΔG is the Gibbs free energy difference between the two minima, given by the ratio of the average dwell times in "0" and "1" states in Fig. 1. In the simplest random free energy models, the distribution of ΔG would be modeled by a Gaussian probability [16]. Tunneling is not expected to play a role at 295 K, but at very low temperatures, tunneling among pairs of minima with $\Delta G \approx 0$ would become important.

Figure 1(a) illustrates that temporally inhomogeneous kinetics was observed for several clusters; i.e., after some hopping back and forth, the two-state system relaxed and the cluster settled in one of the structural minima. The initial rate in Fig. 1(a) is $k_{obs} = 0.13 \pm 0.05$ min^{-1}, calculated from the single cluster dwell times as

$$k_{obs} = \left\langle \frac{1}{\tau(0)} \right\rangle + \left\langle \frac{1}{\tau(1)} \right\rangle, \qquad (2)$$

where $\langle \rangle$ denotes the average. Assuming an exponential distribution of the dwell times $\tau(i)$ in states 0 and 1 shown in Fig. 1(a), the Bayesian likelihood that the rate did not slow during the last 120 min of the movie is only $P < 1\%$.

Ediger and co-workers have observed very heterogeneous dynamics in bulk supercooled liquids near T_g [17]. Our temporal dynamic range (≈ 60:1) is smaller, but we do image direct evidence for spatial heterogeneity (see movie S4 in SI [14]) and temporal heterogeneity [Fig. 1(a) and movie S1 in SI [14]] far below the glass transition. Our direct visualization thus extends heterogeneity to conditions well below T_g.
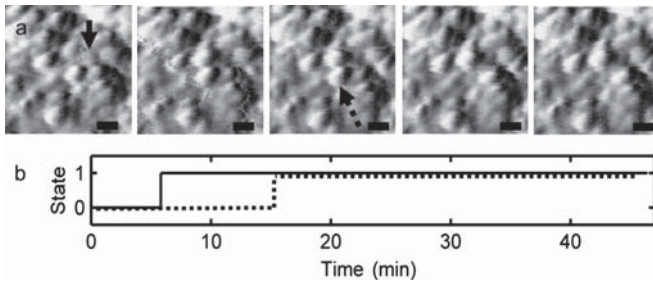
FIG. 3. Concerted motion on *a*-Si surfaces. (a) An ion-bombarded *a*-Si surface on which the hopping of a cluster between frames 1 and 2 (solid arrow) apparently facilitates the hopping of an adjoining cluster between frames 3 and 4 (dotted arrow). See movie S3 in the SI [14]. (b) The corresponding SCT. Scale bar is 1.1 nm = 5 at. diam.

Figure 2 shows the cluster size distribution for both ion-bombarded and vapor-grown *a*-Si surfaces. The average diameter for ion-bombarded *a*-Si is 5.3 ± 1.8 at. diam., and for vapor-deposited *a*-Si it is 4.6 ± 1.2 at. diam. The distribution shown is only for those clusters that moved. The diameter of clusters in Fig. 2 was obtained by averaging the major and minor axis between the ends of clusters in spatial derivative images such as Fig. 1(a). Only the highest resolution images that showed evidence for resolving single Si atoms were used for populating the histogram in Fig. 2. We have observed average diameters of 3–5 atoms for surface clusters of different metallic glasses [12], so an average width of less than about 5 cluster-forming units seems to be universal on these very different glassy surfaces. Indeed, such a diameter has been proposed as the maximum correlation length that can be reached by glasses before the aging process becomes impractically slow [18].

Figure 3(a) demonstrates correlated two-state hopping on an ion-bombarded *a*-Si surface (see movie S3 in SI [14]). Nearby clusters hop in sequence. On a ca 1 nm length scale, motion of one cluster apparently modifies the local free energy surface of a second cluster. We did not observe a single cluster moving between more than 2 states, although we cannot rule out such events with only 13 mobile clusters observed.

a-Si samples are frequently grown with hydrogen incorporated into the structure, especially during CVD [2]. Work by Pohl and co-workers [8] indicated that as little as 1% hydrogen passivation reduces by orders of magnitude the low temperature friction plateau characteristic of glassy dynamics. What is its effect on our observed two-state dynamics?

We find that hydrogen passivation eliminates two-state hopping of *a*-Si surface clusters completely within our dynamic time range on sputtered surfaces, and reduces it on vapor-grown surfaces. To passivate sputtered silicon samples, the samples were kept at   400 °C and exposed to 1 L of hydrogen using a tungsten cracking filament. Figure 4 illustrates the three surface morphologies observed after exposure. The passivated surface showed some crystalline areas 4(d), large blobs of Si 4(e), or cracks 4(f). Taken together, these indicate that H passivation caps the most strained, least bonded Si atoms to lower the surface free energy, thereby reducing two-state dynamics: Cracks indicate that the density of the remaining *a*-Si surface has increased, as expected if strain is relieved. The crystalline patches range from just a few atoms to hundreds of atoms in surface area, and are consistent with a Si(111) surface structure, the lowest energy surface structure for Si. The blobs indicate merging and undercutting of surface structure as a result of reaction with hydrogen. Thus hydrogen passivation has major structural and dynamical consequences. Our observation of missing two-state dynamics upon passivation extends the behavior noted in [8] to room temperature.

Our experiment shows that universal elements of glassy behavior, previously observed in low temperature *a*-Si and on room temperature metallic glass surfaces, are retained at room temperature by the *a*-Si surface, irrespective of preparation method. Among the mesoscopic-kinetic [19]
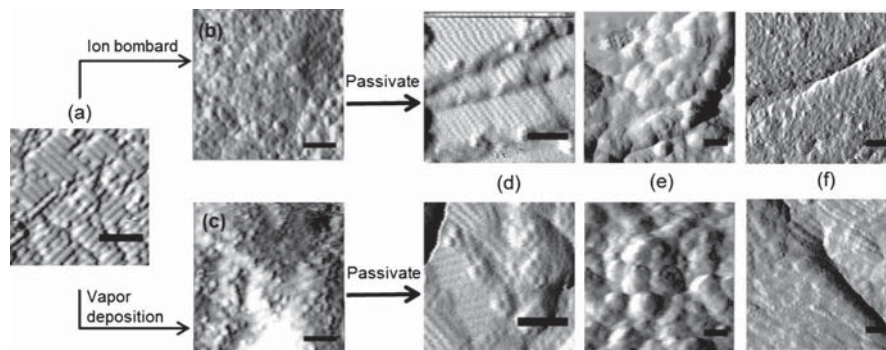

FIG. 4. Generation and quenching of two-state dynamics on *a*-Si surfaces. (a) A crystalline Si(100) 2 × 1 reconstruction which can then be converted to an *a*-Si surface by (b) argon ion bombardment or (c) vapor deposition of *a*-Si on it, generating the two-state dynamics. The dynamics can be quenched by passivating the *a*-Si surfaces with atomic hydrogen. Three topographic changes were observed on both types of surfaces: (d) formation of crystalline patches, (e) formation of large blobs, and (f) formation of rifts. Little unambiguous two-state dynamics was observed on the passivated surfaces. Scale bar is 4.4 nm = 20 at. diam.

and microscopic-thermodynamic models [20] developed for glasses, only the random first order transition model has been extended to glass surfaces so far [21]. It predicts that the activation barrier for compact collective relaxations (α relaxations) decreases by a factor of 2 from the bulk to the surface. The model assumes that surface clusters retain the same size as bulk clusters. With this assumption, the model predicts a barrier of 1.3 eV instead of 2.6 eV for clusters ca 5 atoms in diameter [21]. Our result of 0.93 ± 0.15 eV lies much closer to this predicted surface result than to the bulk value. Some glassy polymer surface experiments also measured much faster surface kinetics than in the bulk [22]. It has been suggested that α relaxation and the much faster localized β relaxation (bulk barrier of 0.77 eV) are just extremes of a continuous distribution of dynamically rearranging units [20]. Our result lies right in the middle of the 0.77–1.3 eV range. It remains to be seen whether glass surface relaxation consists of just one type of motion as observed here, or whether two types of relaxation actually exist. Currently the dynamic range of our experiments is limited, so they would miss much faster or much slower relaxation processes outside the 6–300 min time window.

In conclusion, the STM movies of a-Si reveal only two-state motion of compact clusters. The average size in atomic diameters (5) of these mobile clusters is similar to those observed on several metallic glass surfaces [12] and may be a universal feature for glassy surfaces. A cluster diameter near the predicted bulk value indicates that glassy surfaces have not settled into a lower energy minimum than the bulk because the correlation length is no longer than in the bulk. Therefore simple modifications of bulk glass models, like the factor of 2 reduction in barrier height without consideration of cluster size presented in [21], may be sufficient to analyze glassy surface dynamics. In addition, the a-Si dynamics is spatially and temporally heterogeneous, and occasional correlated two-state hopping is observed. Hydrogenation quenches the two-state dynamics by relaxing the surface to lower energy structures. Thus, our results provide direct evidence for glasslike dynamics on pure a-Si surfaces and its absence on H-passivated surfaces.

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