Evolution of the potential-energy surface of amorphous silicon

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The link between the energy surface of bulk systems and their dynamical properties is generally difficult to establish. Using the activation-relaxation technique (ART nouveau), we follow the change in the barrier distribution of a model of amorphous silicon as a function of the degree of relaxation. We find that while the barrier-height distribution, calculated from the initial minimum, is a unique function that depends only on the level of distribution, the reverse-barrier height distribution, calculated from the final state, is independent of the relaxation, following a different function. Moreover, the resulting gained or released energy distribution is a simple convolution of these two distributions indicating that the activation and relaxation parts of the elementary relaxation mechanism are completely independent. This characterized energy landscape can be used to explain nano-calorimetry measurements.

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The concept of energy landscape has been used extensively in the last decade to characterize the properties of complex materials. In finite systems, such as clusters and proteins, the classification of energy minima and energy barriers has shown that it is possible to understand, using single-dimension representations such as the dis-connectivity graph, the fundamental origin of cluster dynamics and protein folding. For bulk systems, where the relations are more complex, the energy landscape picture has helped further our qualitative understanding of glassy dynamics and of the evolution of supercooled liquids through their inherent structures. Similarly, applied to amorphous semiconductors, it has revealed an unexpected simplicity that suggests universality. In spite of these contributions, many questions remain regarding the evolution of the local structure of the energy landscape itself as a function of relaxation, an evolution that determines the dynamics of disordered materials away from equilibrium. For example, following measurements of heat released during the annealing of damaged generated by low-energy ion implantation in amorphous silicon, it was suggested that the activation energy and the amount of heat released are uncorrelated, microscopic details were still missing, however, as well as a general picture of the phenomenon. Results presented here tie experiments and simulations and provide a clear link between the structure of the energy landscape and experimental observations, supporting the importance of this concept.

More precisely, we focus on amorphous silicon, a model system studied extensively, both experimentally and theoretically, over the years. Using ART nouveau, a saddle-point finding method, we characterize the evolution of the local energy landscape, defined by the distribution of transition states and adjacent energy minima around a local configuration, as a function of relaxation. The resulting theoretical picture can be used to understand and explain recent nano-calorimetric measurements on ion-implanted a-Si samples.

Our a-Si model is relaxed using the Stillinger-Weber potential with parameters adjusted specifically to recover the structural and vibrational properties of the amorphous system. While this potential has a number of shortcomings, its structural evolution as a function of relaxation is in good qualitative agreement with experiments as discussed below. Moreover, it is fast enough to allow for an extensive search of transition states, necessary to construct reliable energy distributions. Starting from a 4000-atom random configuration in a cubic box with periodic-boundary conditions, the system is relaxed using ART nouveau: beginning in a local energy minimum, the system is brought to an adjacent transition state and relaxed into a new minimum. The move is accepted using a Metropolis criterion with a temperature of 0.25 eV, following Ref. The total of 95 445 events is necessary to relax the model from an initial energy per atom of -2.89 eV/atom going down to -3.04 eV/atom (see Fig. in inset). Figure shows the correlation between the energy per atom and the bond-defect concentration (mostly three-fold and five-fold coordinated Si). Following this relaxation, we find a linear relation between the width of the TO peak, calculated using the relation of Ref. and the configurational energy, with a slope of 0.989 (KJ/mol)/deg, in good agreement with experiment.

To characterize the evolution of the local energy landscape as a function of the degree of relaxation, we explore extensively the transition state distributions around four configurations with decreasing internal stress. The energy per atom for these configurations is indicated in Table. From each of these four generic configurations, we generate 100 000 events (exit pathways), providing a detailed picture of the local energy landscape associated with various degrees of relaxation. In each case, we
TABLE I: Properties of the four sampled 4000-atom α-Si configurations including energy per atom and the fitting parameters to Equation 1 for the forward-barrier (FB) distribution.

| C1 | C2 | C3 | C4 |
|----|----|----|----|
| Energy/atom | 2.980 | -2.996 | -3.019 | -3.042 |
| $(E_{FB})$ (eV) | 1.919 | 2.190 | 2.430 | 2.587 |
| $\sigma_{FB}$ (eV) | 1.178 | 1.153 | 1.141 | 1.164 |
| $A$ (eV$^{-2}$) | 0.17 | 0.16 | 0.14 | 0.13 |

FIG. 1: Fraction of coordination defects (mostly 3-fold and 5-fold coordinated atoms) as a function of the configurational energy per atom (in eV) for the 4000-atom model of α-Si. The large circles indicate the location of the four configurations selected for further analysis. Inset: energy per atom as a function of event during the preparation of the configurations.

Even though a system's kinetics is conditioned by the barrier height between minima, the long time evolution of a system is also determined by the overall event energy asymmetry. For example, if system jumps onto a very energetic state, with a high energy asymmetry with respect to the initial minimum, it will come back immediately onto the initial state irrespective of the height of the forward energy barrier. In effect the presence of these highly asymmetric states surrounding a local minimum only slows down the relaxation. To characterize this phenomenon, we plot the reverse energy barrier distribution (Fig. 2(b)), i.e., the energy barrier height measured from the final minimum to the transition state (forward barrier or FB) for configurations C1 to C4. We observe that the distribution is continuous and bounded in agreement with previous simulations [2, 3] but also that it shifts towards higher energy as the configuration are relaxed. As shown in Fig. 3(a), however, the four curves are well represented by the same function given by a Gaussian multiplied by the energy:

$$G_{FB}(E) = AE \exp \left\{ -\frac{(E - (E_{FB})^2)}{2\sigma_{FB}^2} \right\}$$  \hspace{1cm} (1)

where, as is shown in Table I, the peak position controlled by $E_{FB}$ varies with the degree of relaxation but the overall scale $A$ and the width of the distribution, given by $\sigma_{FB}$, are constant. Remarkably, the shift in $E_{FB}$ is significantly larger than the drop in the average strain per atom as the configuration is relaxed: $E_{FB}^{rel}$ shifts by 0.67 eV from C1 to C4 as the energy per atom decreases by only 0.06 eV. This result is consistent with the growing super-Arrhenius relaxation time scale observed in strong glasses and generally described by the empirically-derived Vogel-Fulcher law [13]. However, while this relation postulates a constant energy-barrier and an unusual temperature relation, we see here that the reverse is happening: it is the barrier height that increases with relaxation. The disproportionate shift in the forward barrier distribution as a function of relaxation can be can be explained by previous observations that the defected and strained structures play a major role in the evolution of amorphous systems as diffusion or rearrangement in perfectly coordinated region of the amorphous network tend to have an energy cost similar to the of the crystal [2, 7].

remove the duplicate events leaving about 12 000 different activated pathways from the initial local minimum to a nearby one for each of these four configurations, i.e. about 12 000 different transition points and adjacent minima. The nature of dominant diffusion and relaxation mechanisms in α-Si have already be discussed elsewhere [2, 3] [12] and we focus here on the distribution of forward and reverse barrier heights (measured, respectively, from the transition state to the initial and final state) and energy asymmetry (given by the energy difference between the final and initial state), for each level of relaxation. From previous analysis, we know that although the total number of events in α-Si is between 30 and 60 per atom, the overall distribution converges relatively quickly [4] and we observe only negligible differences in the shape of the various energy distributions by including the events generated after 50 000 or 100 000 ART moves.

From transition state theory, we know that the kinetics of activation-dominated systems is controlled by the rate of escape from the initial energy minimum. Figure 2(a) shows the distribution of activation barriers from the initial minimum to the transition state (forward barrier or FB) for configurations C1 to C4. We observe that the distribution is continuous and bounded in agreement with previous simulations [2, 3] but also that it shifts towards higher energy as the configuration are relaxed. As shown in Fig. 3(a), however, the four curves are well represented by the same function given by a Gaussian multiplied by the energy:

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tion of recurring events is sometimes tricky. Neglecting this region, we see that all backward barrier distributions are represented by the same exponential, \( \exp(-\Delta E/E_0) \), where \( E_0 = 0.60 \text{ eV} \) (see Fig. 3(b)).

These two distributions, forward and backward, cannot be measured directly experimentally. However, the heat released during relaxation is directly associated with the energy asymmetry, i.e., the energy difference between the initial and final minima. Fig. 2(c) shows the energy asymmetry distribution surrounding configurations C1 to C4. The shape of the distribution looks complex, it is a simple convolution of the two independent forward and backward energy barrier distributions, as is shown in Fig. 3(c). Not only do these two distributions behave differently with the relaxation, these turn out to be independent: the height of a barrier does not provide any information regarding the energy of the final minimum.

The energy landscape picture developed here can be used to explain recent differential nano-calorimetric measurements made on implanted \( a-\text{Si} \) \cite{5, 6}, offering an experimental check on these results. Samples are implanted at low temperature and then heated, while heat released is measured, revealing a number of features: First, the heat flux released as the sample is heated is relatively uniform as a function of temperature, for temperatures ranging from 118 to 775 K; second, the stored-strain, measured as the heat rate, saturates as a function of implantation fluence; third, for low fluences, the heat-rate follows nearly the same curve, irrespective of the implantation temperature. For fluences near saturation, the heat release amplitude increases with decreasing implantation temperature. These results were explained by the presence of a continuous distribution of states where each annealing event releases an amount of heat independent of its activation energy. Dynamic annealing was considered responsible for the increasing signal with decreasing temperature near saturation: some configurations are only accessible if underlying, low activation energy configurations survived dynamic annealing.

The saturation of stored-strain can be readily ex-

**FIG. 2:** (a) Forward and (b) reverse energy-barrier distribution, and (c) asymmetry energy distribution for configurations C1 to C4.

**FIG. 3:** Collapsed (a) Forward and (b) reverse energy barrier distributions, following the equations given in the text. (c) Asymmetry distribution for configuration C2 and the corresponding distribution generated by convoluting the respective forward and reverse barrier distributions.
plained within the context of energy landscape: We have seen that the barrier-height distribution shifts to lower energy as the strain level increases. As this shifts occurs, the number of barriers within $k_BT$ increases reaching a point, for a given temperature, at which relaxation takes place faster than the strain increase, leading to the saturation.

Understanding the behavior of the released heat-flux requires more analysis. For this, we suppose that since the energy-barrier distribution shifts rapidly to higher energy as the system is relaxed, low-energy barriers are independent, heat released after ion-implantation is proportional to the number of barrier crossed, which increases linearly with the temperature, for highly disordered systems, and flattens out for more relaxed configurations, where the impact of the exponential reverse barrier distribution becomes more important. Moreover, the rapid shift in the forward-energy barrier distribution as a function of relaxation also explains the saturation in stored strain at high fluence. While it remains to be confirmed numerically, the picture developed here should apply to covalent glasses in general.

In conclusion, a detailed analysis of the evolution of the energy landscape for model α–Si shows features that provide a clear picture of defect relaxation in support of recent differential nano-calorimetric measurements. Because the forward and reverse energy barrier distributions are independent, heat released after ion-implantation is proportional to the number of barrier crossed, which increases linearly with the temperature, for highly disordered systems, and flattens out for more relaxed configurations, where the impact of the exponential reverse barrier distribution becomes more important. Moreover, the rapid shift in the forward-energy barrier distribution as a function of relaxation also explains the saturation in stored strain at high fluence. While it remains to be confirmed numerically, the picture developed here should apply to covalent glasses in general.

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