Athermal Activation in Glassy Fluid

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Abstract

In this article, the mechanism of the unexpected high fluidity in SiOx nanowire under modest irradiation was proposed, the high fluidity is attributed to the long lifetime of irradiation-induced holes, which arise from formation of small polarons. The holes created in irradiation could have a long lifetime, and localized in space, such missing of bonding electron could suppress the energy barrier (athermal activation effect) for a Pachner move of the network. The atomic level dynamics of the system is proposed by interaction of phonon and local configuration, the activation effect was then studied with passing rate of corresponding stochastic dynamic equation, calculation shows an exponential dependent of the time-lapse of Pachner move to lifetime of the activation, furthermore, connection between the local configuration time and viscosity of the fluid indicates a strong sensitivity of viscosity to lifetime of the athermal activation, such mechanism would give an effective interpretation to the unexpected high fluidity together with the passivation effect of the conductor on the material.

Benefit from the advance in the observation technique in electron microscopy, atomic observation of material had been achieved [1–6], however, with such high resolution, the beam-induced phenomena would mix up with the intrinsic nature of the material in in-situ observation, in this way, the beam-induced phenomena have attracted wide research and discussion [7–9], these beam-induced phenomena can also enlighten invention of new technology like nano-fabrication and processing. In recent years, in the investigation of nano-welding with in-situ electron microscopy (HRTEM) observation, beam-induced atoms migration has been observed and described [10–13]. In these investigations, the massive fluid-like migration of atoms in the SiOx nanowires under modest irradiation was observed, where the viscosity of such flow under a certain dose rate of electron beam irradiation [13] could be estimated to be $10^{12} Pa \cdot s$ with the assumption of the invariance of the surface tension, the estimated viscosity was to the viscosity of fused silica which is heated to above 2000K, and such high temperature is believed to be un-attainable in HRTEM observation. The fluidity induced by irradiation was further observed to be passivated by pre-deposited metal nanoparticle [12], in which the nanowire show much less fluidity when pre-deposited with gold nanoparticle under the same irradiation dose rate.

The conventional consideration of beam damage [8, 9] could not offer a detailed interpretation of the observed high fluidity. In the existing discussion, the damage can be divided into
either irradiation-ion interaction or irradiation-electron interaction, the first is characteristic with knock-on mechanism\cite{7,14} where the ion in the material is bombarded by the irradiation and exist the material or dislocated in the lattice with momentum transferred by the incoming irradiation. The second is always referred to as the radiolysis, and the sequential reconstruction of atoms\cite{15}. Accumulation of heat and charge can also be induced in the above interaction. However, in these considerations, only the long-lived localized damages have been taken into detailed discussion, while they could be observed either directly in HRTEM or the ordinary spectrum observation, however, localized unstable excitation can also be created in the irradiation. The effect of such excitation is unable to be analyzed with conventional thermal dynamic methods based on equilibrium, but the following illustration would show that there could be intriguing phenomenon which comes out of such excitation.

In materials science, as the valent bond electrons form chemical bonds to transfer momentum between ions, and the mass of the electron is about $1/10000$ the mass of the ion, when we are dealing with the mechanical response of materials, in often cases we do not have to come to the level of the electron to deal with the problem, that is, in the solid, the relaxation time of electron is much lower than that of ion, in the region of mechanical response, the interaction of atoms can be dealing with an elastic potential, however, there could be some extreme cases where the relaxation time of electron is slowed to the scale of relaxation time of ions, the elastic potential model under such circumstance would come to a failure, the long-life excitation state could have a great influence on the mechanical response of materials.

Specifically in the SiO$_x$ nanowires, in the irradiation, the electron in the material can be directly knocked or emitted through Auger effect, while in the nanoscale material, the electron deposited in the irradiation will be less than the electron loss in the irradiation, the net charge accumulated would be positive after irradiation\cite{9}. The positive charge accumulated in the irradiation would be holes in the energy band of the material, these holes created in the irradiation would be localized in lattice and have little contribution to the conductance through formation of small polaron, the existence of such holes have been proved through electron spin resonance(ESR)\cite{16}, and the lifetime is observed to be extended to atoms vibrational timescale\cite{17}, the localized holes should influence the chemical bonds in the shading area, and the long lifetime of such excitation would enable the influence to mechanical response, the losing of bonding electrons should have a suppressing effect on the
atomic interaction force, to quantify the influence on dynamics of local configuration and the further mechanical response of the material, the phonon-local configuration interaction should be introduced.

In the silica, the atoms are tightly compact, and in such a situation, the dynamics could be established with the phonon as an ingredient. For an atom in the material, the position can be expressed with the summarization of amplitude of phonons, by choosing the local coordinate and only consider in the direction connecting two local equilibriums, in 3 dimension lattice, two T mode and one L mode phonon contribute to the transition, the donation of each mode with different wavelength should be different, nevertheless, the local vibration mode in high frequency should have less donation for the spacial exponential decay, all these effects are included into the response modification function $q(\omega_i)$, and in the neighborhood of local equilibrium:

$$ x \propto \sum_i q(\omega_i)e^{-\frac{\hbar \omega_i}{kT}} \cos (\theta_i) $$

(1)

Where $\hbar \omega_i = \frac{k^2}{2m}$ and $\theta_i$ is the phase which could be considered to be uniformly distributed in $[0, 2\pi)$. For each component $\omega_i$, the standard derivation is finite, apply the central limit theory, the distribution of $x$ turns to be a Gaussian distribution.

$$ P(x) \propto e^{-\frac{m\omega^2 x^2}{2kT}} $$

(2)

Where $m\omega^2$ is associated with the standard deviation of the distribution of $x$. Applying that $\frac{\partial \theta_i}{\partial t} = \omega_i$, the velocity of the atom is:

$$ \dot{x} \propto \sum_i \omega_i q(\omega_i)e^{-\frac{\hbar \omega_i}{kT}} \sin (\theta_i) $$

(3)

And such distribution is Gaussian too:

$$ P(\dot{x}) \propto e^{-\frac{m\dot{x}^2}{2kT}} $$

(4)

The average of $x$ and $\dot{x}$ will be:

$$ \langle x \rangle = 0 $$

(5)

$$ \langle \dot{x} \rangle = 0 $$

(6)
And the covariance of $x$ and $\dot{x}$ will be:

$$cov(x, \dot{x}) = \int_0^{2\pi} \prod \frac{d\theta_i}{2\pi} \omega_j \sum_{i,j} e^{-\frac{\bar{h}(\omega_i + \omega_j)}{kT}} q(\omega_i)q(\omega_j) \cos(\theta_i) \sin(\theta_j)$$

$$= 0 \quad (7)$$

So, the joint probability distribution can be separated, the distribution function of velocity should be a Gaussian distribution independent from the position. By adding up to the potential which corresponding to the non-harmonic part of the total interactive potential $U(x)$, we can construct the random dynamic equation:

$$\frac{\partial x}{\partial t} = -\tau \frac{\partial U(x)}{\partial x} + \sqrt{\frac{2}{m}} B(t) \quad (8)$$

$$\langle B(t) B(0) \rangle = k_B T \delta(t) \quad (9)$$

Where $B(t)$ is a white noise function that fulfills Gaussian distribution, which arises from the momentum transfer by the phonon, and $\tau$ is a constant which has the unit of s. This equation is the famous Smoluchowski differential equation, which describes the dynamics of a molecule in a potential field with strong damping, such strong damping arises from the fact that the velocity of atoms is always much slower than the speed of sound in the material.

The activation effect in the irradiation can be easily introduced to this model by modulating the potential with a stepped function. For one dimension problem, the corresponding potential is simple:

$$U(x, t) = U(x) f(t) \quad (10)$$

$$f(t) = \begin{cases} \lambda & 0 \leq t < t_a \\ 1 & t_a \leq t < T_a \end{cases} \quad (11)$$

Where $\lambda$ is the activation coefficient and $T_a$ is the average time lapse between two activation events. The force field corresponding to the potential is chosen to be piecewise parabolic:

$$F(x) = \begin{cases} -k_s(x - x_s) & x \leq 0 \\ -k_u(x - x_u) & x \geq 0 \end{cases} \quad (12)$$
The lower labels $s$ and $u$ correspond to stable balance point and unstable balance point, the factor $k_s > 0, k_u < 0$.

A universal method of path integral in such cases is provided in Refs. [18], such method based on the saddle point approximation that the fluctuation is relatively weak, in our case, the temperature in the experiment observation should be in room temperature range, and such temperature is relatively low for dynamics of atoms in silica.

Through the path integral method, the passing rate $\Gamma(t)$ is:

$$\Gamma(t) = \int_{t_0}^{t} dt_1 \frac{Z(t, t_i)}{D} e^{-\Phi(t, t_i)/D}$$  \hspace{1cm} (13)

In which:

$$D = \frac{\tau k_B T}{m}$$ \hspace{1cm} (14)

$$\Phi(t, t_i) = -\frac{x_u^2}{2I_u(t, t_i)} + \frac{x_s^2}{2I_s(t, t_0)}$$ \hspace{1cm} (15)

$$Z(t, t_i) = \frac{[Y(t_i) - x_s]x_u}{2\pi(I_u(t, t_i) I_s(t_i, t_0))^{\frac{1}{2}}} e^{2\Lambda_u(t, t_i)}$$ \hspace{1cm} (16)

$$Y(t_i, t_0) = k_s x_s I_s(t_i, t_0) f(t_i)$$ \hspace{1cm} (17)

$$I_s(t_i, t_0) = 2 \int_{t_0}^{t_i} dt' e^{2\Lambda_s(t_i, t')}$$ \hspace{1cm} (18)

$$\Lambda_s(t_i, t) = -\int_{t}^{t_i} dt' k_s f(t')$$ \hspace{1cm} (19)

$$I_u(t, t_f) = 2 \int_{t_f}^{t} dt' e^{2\Lambda_u(t, t')}$$ \hspace{1cm} (20)

$$\Lambda_u(t_i, t) = -\int_{t}^{t_i} dt' k_u f(t')$$ \hspace{1cm} (21)

Numerical calculation of passing rate $\Gamma(t)$ is shown in Fig. 1, the result is shown in logarithmic scale, the passing rate changes exponentially shortly after the activation enters or leaves, and gradually saturates to the corresponding Kramers rate. The most important parameter is the average passage time, which is corresponded to the average time for a Pachner move in the network of atoms, is a function of passing rate:

$$\bar{t}_p = \frac{T_a}{\int_0^{T_a} dt \Gamma(t)}$$ \hspace{1cm} (22)

The integral is calculated numerically and the result is shown in Fig. 2 we can see that $\bar{t}_p$ show very small plateaus in low activation lifetime and gradually flattening in high activation...
FIG. 1. Diagram of passing rate $\Gamma(t)$ in logarithmic scale, the calculation was performed with $D = 0.04, k_s = -k_u = 1, x_u = -x_s = 1, t_0 = -10, \lambda = 0.2$ and $t_a = 1, 4, 12, 22$, the system reached local-equilibrium in $t = 0$, two Kramers rate is noted with dot line.

lifetime, while an exponential decrease lies in between, in this region, the average reaching time will be strongly affected by a small change of activation timescale resulted from the exponential increasement of $\Gamma(t)$, after $\Gamma(t)$ saturates to Kramers rate, with the increase of the activation lifetime, $\bar{t}_p$ decrease with increase of weight of activation, and such increase would be smoother than the exponential decrease. Furthermore, the divergence between the two Kramers rate would increase with decrease of temperature, that is, the system would behave more abnormal in lower temperature.

The connection between a timescale variable describes the atomic movement with the viscosity of the material is generally discussed\textsuperscript{19, 20}, the definition of viscosity is associated with a Maxwell relaxation time $\tau_M$:

$$
\tau_M = \frac{\eta}{G_{\infty}}
$$

(23)

Where $G_{\infty}$ is the infinite frequency shear module and in strong glass like fused silica glass in this case, $\tau_M \propto \tau_{LC}$; the $\tau_{LC}$ is the time of local configuration, and $\tau_{LC} \propto \bar{t}_p$, while the divergence of $\tau_M$ with $\tau_{LC}$ only happen in fragile glass, the viscosity of the activated material should be:

$$
\eta_a = \frac{\bar{t}_p}{t_0} \eta_0
$$

(24)
FIG. 2. Diagram of average passage time $\bar{t}_p$ with logarithmic scale, $T_a = 1000$ and other parameters are the same as Fig.1, a small plateau shows in the first stage, the curve further saturated with increase of $t_a$, the plateau in the early stage is shown in top right.

In which $t_0$ is the corresponding pristine average passing time in the non-activated case. Such relation indicated that change of viscosity by activation can be easily observed in rheology experiment.

In the experimental scenario, the non-exponential dependence of time-lapse of activation $T$ indicates the activation effect cannot be exponentially suppressed by the density of holes instead of the lifetime of holes, which means the dose of irradiation would not serve to be a threshold in the changing of viscosity. And the lifetime of holes created by irradiation could be suppressed by the mutual repulse interaction, electric field induced by accumulation of charge, interaction with phonon, and nearby free-electron donator, this explains the passivation effect of pre-deposited conductor nanoparticle observed in the experiment.

The low viscosity observed in the irradiated SiOx nanowire cannot be simulated through the conventional ab-initio way, because the most practical method in the simulation was based on the Born-Oppenheimer approximation, the exact trajectory of carrier wave function along the time axis is neglected, and in the most cases, such approximation works well. But in some cases, like solving the movement of light atoms like hydrogen in the water molecule, such approximation show observable diversion with the fact\cite{21}, furthermore, this paper proposes a new scenario where the approximation breaks, the movement of electron could be localized and slowed to scale of the movement of atoms, the dynamics of atoms could be strongly influenced by the lifetime of the electron.
In the article, the beam-induced fluid-like migration of atoms is interpreted with athermal activation effect in local configuration-phonon interaction, further calculation shows an exponential dependence of the local configuration lifetime with activation lifetime, this offers a good interpretation to the passivation effect of the pre-deposited metal nanoparticle. The ultra-sensitivity to the lifetime of the activation indicates that there could be some irradiation protect mechanism where the irradiation damage is eased by decreasing the lifetime of the excitation when the fluctuation is the meaning driving force of structural reorganization, especially in the biomaterial like DNA.

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