Suppression of β Relaxation in Vapor-Deposited Ultrastable Glasses

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Glassy materials display numerous important properties which relate to the presence and intensity of the secondary (β) relaxations that dominate the dynamics below the glass transition temperature. However, experimental protocols such as annealing allow little control over the β relaxation for most glasses. Here we report on the β relaxation of toluene in highly stable glasses prepared by physical vapor deposition. At conditions that generate the highest kinetic stability, about 70% of the β relaxation intensity is suppressed, indicating the proximity of this state to the long-sought "ideal glass." While preparing such a state via deposition takes less than an hour, it would require ~3500 years of annealing an ordinary glass to obtain similarly suppressed dynamics.

At sufficiently high temperatures, structural relaxation in a liquid is governed by a single process [1–3], whereas dynamics in supercooled liquids split into primary (α) and secondary (β) relaxations [1–5]. Below the glass transition temperature T_g, the α relaxation is frozen but the β relaxation persists in the glassy state, thus becoming the principle source of dynamics in glassy states. The Johari-Goldstein (JG) type of β relaxation is particularly important, because it is an inherent feature in glass-forming materials [4–6]. Some NMR measurements indicate that β relaxations are cooperative in nature [7] and involve the motion of essentially all the molecules [8,9]. The β process is related to local atomic motions and is of practical significance to many properties of glassy materials [2,4,5]. For example, the β relaxations have been identified to correlate with the basic units of plastic deformation [10] and are utilized to enhance mechanical ductility of metallic glasses [11]. The β relaxation also plays a critical role in determining protein stability in sugar-glass matrices [12]. Meanwhile, the microscopic mechanism of β relaxations is not clearly established, and it represents substantial challenges for theory, simulation, and experiment [4,5,13,14]. It is anticipated that the ability to tune β relaxations, without involving a change of chemical structures, would provide important insights to this long-standing issue.

For most glassy materials, β relaxations are relatively insensitive to external treatments and are thus not easily modified. Annealing represents the most commonly used approach in the attempt to tune β relaxations, but it reduces the intensity (i.e., height of the peak) only by ~10% within typical experimental time scales (e.g., Refs. [15–17] and Table SI [18]). Extrapolating such data for a broad range of materials, it would require thousands to millions of years of

annealing to reduce the intensity of the β process by a factor of 3 (Table SI [18] and Refs. [19–32]).

Recently, novel glasses that exhibit remarkable stability have been prepared by physical vapor deposition [33]. The key recipe for the formation of such ultrastable glasses is to deposit the materials at substrate temperatures around $0.85T_g$. This allows molecules to utilize surface mobility and rearrange towards configurations with lower enthalpy [34]. These glasses have properties such as density, elastic modulus, enthalpy, and specific heat, which would otherwise be obtained only if ordinary glasses were annealed for thousands of years [33,35,36]. The main focus of this work is to explore the β relaxation in such highly stable glasses. This is of crucial importance for both revealing the origin of the β relaxation in glassy materials and improving our understanding of ultrastable glasses.

We selected toluene (C_7H_8, with $T_g = 117$ K) as a model material because of its simple chemical structure and especially because its well-characterized β relaxation originates from purely intermolecular interactions, i.e., from a genuine JG-type β relaxation [37]. We performed *in situ* dielectric measurements to probe the relaxation dynamics of glasses that were vapor-deposited onto a high-precision, microlithographically fabricated interdigitated electrode cell using an ultraprecision capacitance bridge [Figs. 1(a) and 1(b)] [17]. Experimental details are presented in Supplemental Material [18].

Figure 1(c) shows the dielectric loss spectra of a toluene glass deposited at a substrate temperature $T_{sub} = 98$ K ($=0.84T_g$), a condition known to form ultrastable glass [38]. The most prominent feature is the low intensity of dielectric loss for the as-deposited glass (run 1 in Fig. 1). Compared with the subsequent two measurements taken after conversion to the ordinary supercooled liquids (runs 2
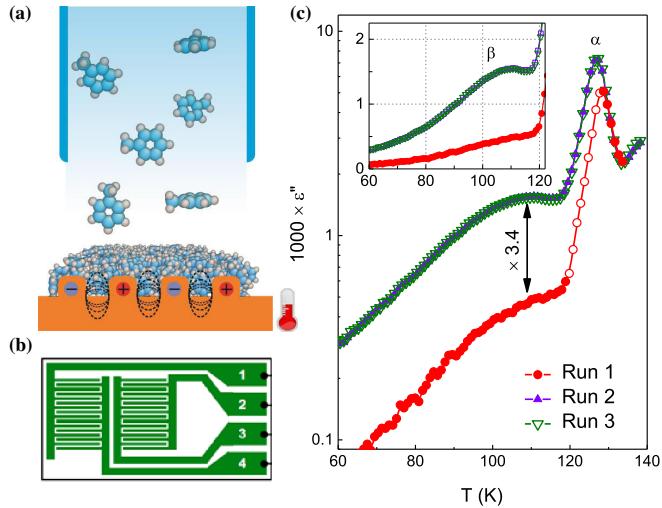
FIG. 1 (color online). Dielectric measurements of vapor-deposited toluene glass. (a) Schematic drawing of the vapor-deposition procedure. (b) Outline of the interdigitated electrode structures used for the dielectric measurements. (c) Dielectric loss spectra ε'' (at test frequency $f = 1$ kHz) of toluene deposited at $T_{sub} = 98$ K and deposition rate 0.4 nm/s.

and 3, nearly superposed), the β relaxation of the deposited glass (the broad peak around 110 K) is drastically suppressed. Quantitatively, the intensity of β relaxation in terms of its ε'' value near the peak is suppressed from 1.6×10^{-3} in the ordinary glass (OG) to 4.7×10^{-4} in the as-deposited stable glass (SG), which corresponds to a factor of 3.4. This remarkable difference between the dynamics in the SG and the OG indicates that 70% of the β relaxation amplitude ($\Delta\varepsilon_\beta$) can be suppressed in the SG, a reduction that has never been observed by physical aging for any glassy material (Table SI). This indicates the proximity of this ultrastable state to that of the ideal glass, where all relaxations have ceased and $\Delta\varepsilon_\beta = 0$.

We note that the peak around $T = 129$ K for the first measurement (run 1) in Fig. 1 does not represent the α relaxation of the deposited glass. Instead, the steep rise of ε'' in the $T = 120$–129 K range (open circles) originates from the conversion from the deposited glass to the ordinary supercooled liquid (see also Fig. S2). Therefore, only after the conversion is completed ($T > 129$ K) do the ε'' values of run 1 coincide with those of runs 2 and 3.

Apart from the suppression of the intensity of the β relaxation, a closer scrutiny of the dielectric loss in isochronal measurements reveals that the SG displays a higher peak temperature of the β relaxation (Fig. S3), equivalent to a reduced peak frequency in isothermal loss spectra. As seen in Fig. 2, this temperature difference (~ 7 K) corresponds to one order of magnitude disparity in the β relaxation time τ_β; i.e., the τ_β of the SG is about 10 times slower than that of OG. Figure 2 reports the temperature-dependent characteristic relaxation times τ in an
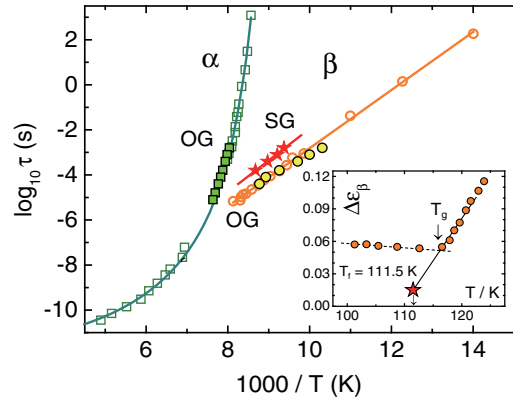

FIG. 2 (color online). Logarithmic relaxation times of α and β processes of ordinary glass (open symbols, from Refs. [39,40]) and the relaxation times for the present vapor-deposited samples (solid symbols) vs reciprocal temperature. Inset: The intensity of the β relaxation peak as a function of temperature for ordinary glass (circles) and that extrapolated to ultrastable glass (red star).

Arrhenius representation [39–41]. Both β relaxations in the OG and the SG can be fitted by an Arrhenius relation $\tau_\beta = \tau_0 \exp(E_\beta/RT)$, with the activation energy $E_\beta = 25 \pm 2$ and 27 ± 3 kJ/mol, respectively. From the perspective of potential energy landscapes, this reveals that basins deep in the potential energy landscape (responsible for the β relaxation) are separated by barriers with similar height to those in ordinary glasses, even though the barriers between metabasins (responsible for α relaxation) are much larger.

Figures 3(a) and 3(b) summarize how the suppression of β relaxation [based on loss values of the deposited and ordinary glass, $(\varepsilon''_{SG} - \varepsilon''_{OG})/\varepsilon''_{OG}$, at the peak position] depends on the substrate temperature T_{sub} (with fixed deposition rate ~ 0.4 nm/s) and on the deposition rate (with fixed substrate temperature $T_{sub} = 98$ K). First, Fig. 3(a) shows that deposited glasses with reduced β relaxation can be prepared in a wide range of T_{sub}, from about 30 to 120 K corresponding to $0.25T_g$ to near T_g. The most effective temperature range is between 0.6 and $0.9T_g$, where the magnitudes of suppression are above a factor of 3. Second, Fig. 3(b) shows that, while the suppression of β relaxation can be tuned within a wide range of deposition rates (0.1–100 nm/s), there is a critical rate about 1 nm/s, below which the suppression of β relaxation no longer depends on the deposition rate.

Figures 3(a) and 3(b) also include the nanocalorimetry heat capacity data of Ahrenberg et al. [38]. One can observe that the present dielectric measurements and the heat capacity results have similar T_{sub} and deposition rate dependence; i.e., the relative changes are practically proportional. Especially notable, the temperature range with the largest suppression of the β relaxation coincides with the most stable region as reflected by the diminished heat capacity [Fig. 3(a)]. Also, the critical deposition rate
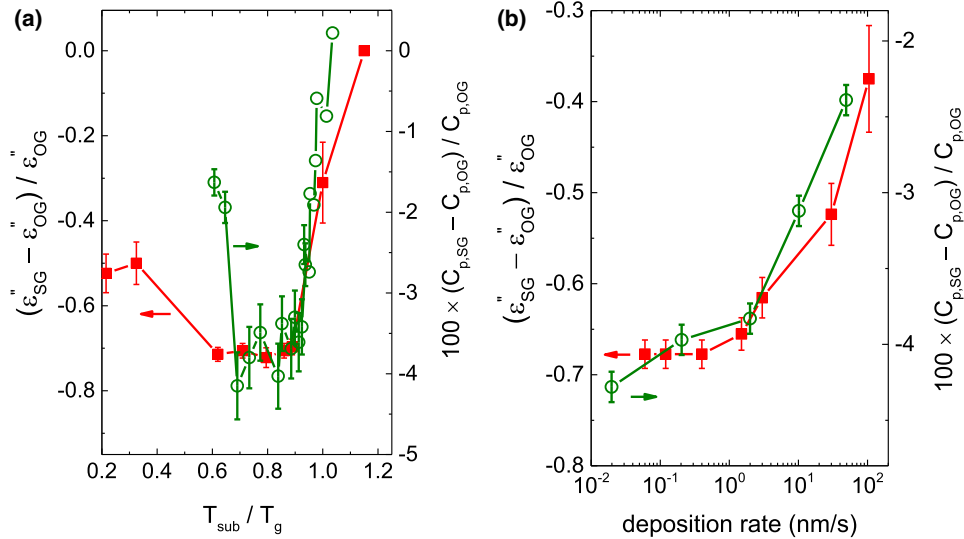
FIG. 3 (color online).   Tuning the intensity of the β relaxation by deposition parameters. The suppression of the relative intensity of the β relaxation (solid symbols) in terms of its dependence on (a) substrate temperature T_{sub} scaled to $T_g = 117$ K (at a deposition rate of ~ 0.4 nm/s) and (b) deposition rates (at $T_{sub} = 98$ K). The heat capacity data (open symbols, right axis) are taken from Ahrenberg *et al.* [38].

determined from the two methods is consistent, as shown in Fig. 3(b). Because the diminished heat capacity is correlated with the kinetic stability [38], the suppression of the β relaxation should also be related to kinetic stability. While the variation of $C_{p,SG}/C_{p,OG}$ with deposition conditions has been linked to changes in vibrational degrees of freedom [38], a direct contribution to the glassy state C_p from the β process of toluene may be responsible for the approximate proportionality of $(\varepsilon''_{SG} - \varepsilon''_{OG})/\varepsilon''_{OG}$ and $(C_{p,SG} - C_{p,OG})/C_{p,OG}$ shown in Fig. 3 (see Refs. [42,43]).

How does the suppression of the β relaxation in vapor-deposited ultrastable glasses compare with results from annealing OGs? To answer this question, we annealed a liquid-cooled toluene glass at 110 K. From the dielectric spectra shown in Fig. 4(a), one can discern that the peak intensity decreases gradually with annealing; however, the remaining intensity is still about 80% of its initial amplitude after annealing as long as 210 h. Such a rate of β amplitude reduction agrees with results of other glassy materials (Table SI [18]). Extrapolating the intensity of the β relaxation with annealing time, as shown in Fig. 4(b), we find that the OG would require at least 3500 years of annealing to achieve the 70% intensity reduction as observed in the SG. This is consistent with previous estimates that SGs have properties that would require aging OGs for times in excess of thousands of years [38,44].

According to the NMR studies of Vogel and Rössler [8,9], the β relaxation of toluene is best described by molecular reorientations limited to a certain cone angle. The relevant cone angles χ are subject to a distribution, characterized by a continuous probability density in the $\chi = 2°$–$10°$ range that accounts for 90% of the molecules,

with additional contributions at $\chi = 40°$ and $50°$ that account for the remaining 10%. Assuming that the contribution to the dielectric loss scales as $\sin(\chi)$, the few molecules associated with large cone angles could contribute about 50% of the dielectric relaxation amplitude.
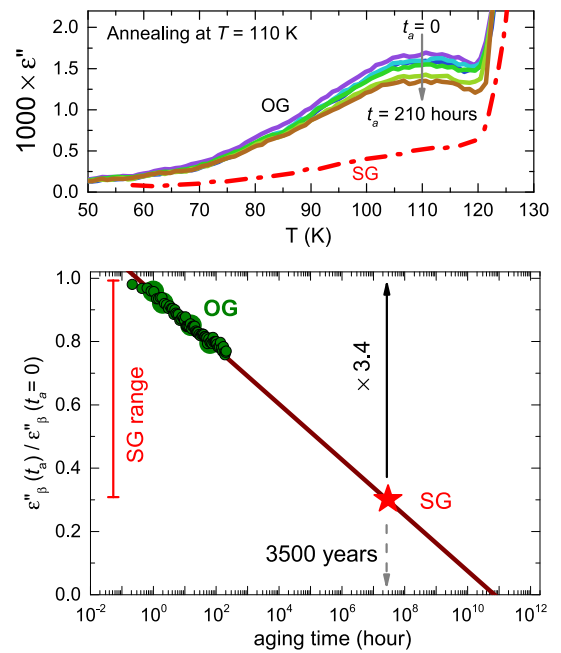

FIG. 4 (color online).   The intensity of β relaxation during annealing for the ordinary glass. (a) The solid lines are dielectric loss spectra of ordinary glasses annealed at $T = 110$ K, and the annealing time is 0, 1, 4, 15, 63, and 210 h from top to bottom. The dashed line is for the ultrastable glass. (b) The normalized intensity of the β relaxation as a function of annealing time.

Therefore, much of the β intensity reduction in the ultra-stable state might originate mainly from eliminating the large cone angles, although a uniform limitation of cone angles (by a factor of 2–3) through overall improved packing efficiency is also possible.

As reported by Kudlik *et al.* [39], the β relaxation of toluene shows a considerable reduction in amplitude with decreasing temperature in the equilibrium supercooled state (for $T > T_g$). Extrapolation of these $\Delta\varepsilon_\beta$ (T) data to a factor of $1/3.4$ of the glassy state level suggests that the SG has properties expected if the material were in equilibrium at about $T = 111.5$ K (see the inset in Fig. 2). This is expressed by the concept of a fictive temperature using $T_f = 111.5$ K for the ultrastable glass, which is similar to the value of 111 K obtained from the enthalpy by Sepúlveda *et al.* [45] for the same material. Extrapolating the relation for T and τ_α in Fig. 2 to $T = T_f = 111.5$ K results in a structural relaxation time of around 10^4 years, in reasonable agreement with the 3500 year age obtained from the β suppression data [Fig. 4(b)]. This indicates that α and β dynamics reveal a consistent thermodynamic state for the ultrastable state.

Finally, we note that our findings here are not limited to toluene glasses. We have observed similar behavior for glasses of *n*-propanol and 2-picoline. The suppression of β relaxations could be a universal phenomenon in ultrastable glasses. Our results thus indicate a general approach to suppression of β relaxations in glassy materials, which could be utilized in tuning properties, such as to tailor the mechanical properties of ultrastable metallic [46] and polymer [47] glasses or glasses used in organic electronics [48]. Vapor-deposited glasses also offer new benchmarks to study the origin of β relaxations.

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