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Mechanisms of photoinduced fluidity in chalcogenide glasses: Molecular orbital analyses

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ABSTRACT

Atomic processes giving rise to the photoinduced fluidity have been studied for amorphous selenium. Ab initio molecular orbital calculations of Se clusters suggest that distorted atomic structures such as curled and intersecting chains have smaller optical gaps. Those atomic sites are likely to be excited by subgap (Urbach-edge) light, which undergo structural relaxation including bond breakages and interchanges. Such photo-electro-structural transformations could originate the macroscopic fluidity. Possibility of electronic glass-transition is also discussed.

1. Introduction

Glassy materials are known to behave fluidly under electronic excitations, the fact being reported by Vonwiller for Se about a century ago [1]. Recent studies have demonstrated that such fluidity $f (= 1/\eta)$, where η is the viscosity) appears also in SiO₂ at temperatures substantially below the glass-transition temperature [2]. Besides, Se, As₂Se₃, As₂S₃ and Ge–Se exhibit photoinduced fluidity¹ at low temperatures [3–8], which manifests its athermal nature. We may then regard that the phenomenon is a kind of “electronic melting”, observed in crystals under intense, pulsed light exposures [9–11]. Nevertheless, it should be emphasized that the fluidity in glasses is conspicuous under moderate excitations. Specifically, in the chalcogenide glasses with bandgap energies of ~ 2 eV [12], the fluidity of $\sim 10^{-12}$ P⁻¹ appears during illumination of subgap photons, or so-called Urbach-edge light possessing absorption coefficients of $1\text{--}10^4$ cm⁻¹, emitted from 10 mW-class cw lasers [4–8]. In applications, this phenomenon has potential for optical micro-fabrication [8,13]. Also, the fluidity in combination with several kinds of motive forces is able to produce permanent photoinduced deformations [14,15], which may be promising to make optical devices such as micro lenses [15] and polarization-controlled structures [16]. However, why the glass exhibits the

electronically induced fluidity remains speculative.

We here focus upon amorphous (a-) Se as the simplest example, with a schematic atomic view being given in Fig. 1(a) as a reference [12]. The structure is composed only with –Se–Se– homopolar bonds, which probably form (deformed) rings and entangled chains, the ratio naturally depending upon preparation procedures [17]. In the meta-stable structures, however, the short-range order, i.e. the coordination number $Z (= 2)$, bond length $r (\approx 2.3 \text{ \AA})$ and bond angle $\theta (\approx 105^\circ)$, is mostly preserved, with some disorder in the dihedral angle φ and the inter-chain distance R [18,19]. A single chain may be longer than 10^5 in the atom number [12,18]. Native defects such as C₃ (three-fold coordinated chalcogen) could also exist, though the estimated density might be too few to directly affect mechanical properties [12].

We note here that such a structure as in Fig. 1 resembles those in organic polymers, a typical substance being polyethylene PE, comprising of –CH₂–. For its amorphous states, substantial studies on atomic motions have been performed, which develop principal concepts such as the Rouse and the reptation model [20–24]. Hence, those outcomes could give insights into the dynamics of a-Se.

Nevertheless, we should also mark two characteristic differences between the organic and inorganic polymers: one is the bond strengths. For instance, the Pauling's bond energies for C–C and Se–Se are 3.6

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E-mail address: keiji@eng.hokudai.ac.jp (K. Tanaka).¹ The phenomenon that a chalcogenide glass becomes fluid during (not after) exposures to light has been termed in several ways, such as photoinduced stress-relaxation [7] and viscosity [6,14], which are unified into “fluidity” in the present work.<https://doi.org/10.1016/j.jnoncrysol.2017.12.005>

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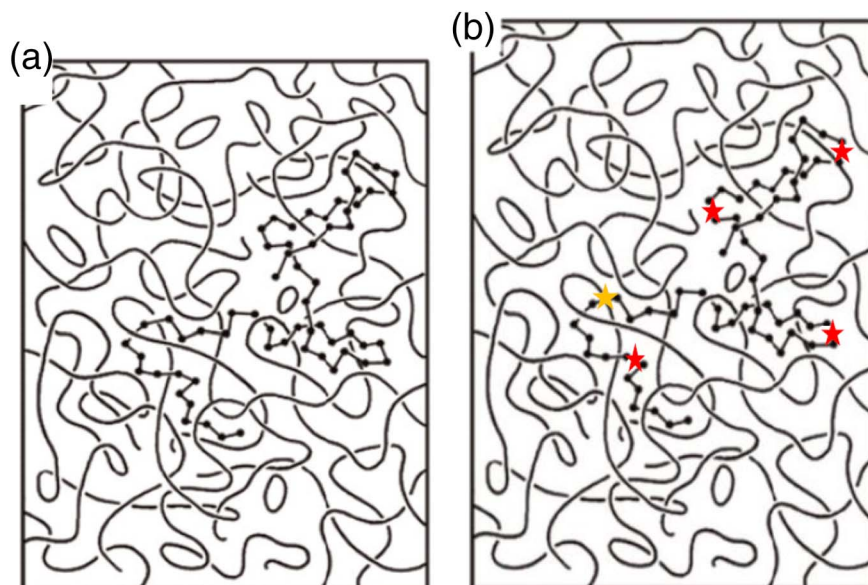


Fig. 1. An entangled chain/ring structure of a-Se [12], in which the atoms are depicted only on a single chain for simplicity. (a) shows an annealed state, and (b) its structure under a vertical stress (exaggerated) and illumination, with the red and orange stars representing excited sites, which may undergo bond breakages and intersections, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and 1.9 eV. Besides, the inter- and intra-molecular distance ratios R/r in PE and Se are ~ 3.3 ($\approx 5/1.5$ Å [21,23]) and ~ 1.5 ($\approx 3.7/2.4$ Å [18,19]). In PE the intra- and the inter-molecular characters are distinctly different, and accordingly, chain crossing upon structural changes cannot be a common process [20,22,24], which may not be the case in liquid Se [25] (and also in liquid S [26]). The other regards the electronic structures. In contrast to the sp^3 -type valence-electron configuration of C atoms in PE, Se atoms in the C_2 (two-fold coordinated) bonding retain the p^4 -like wavefunction, which splits into the σ , π , π^* , and σ^* states. In many Se clusters, these π^* and σ^* states form the HOMO and LUMO levels, which in the elemental lone-pair (LP) electron semiconductor [12], solid Se, constitute the edges of the valence and the conduction band with the optical gap of ~ 2.0 eV [18].

When a-Se as in Fig. 1(a) is illuminated under stresses, what kinds of atomic motions occur? It might be assumed that the stress produces elastically-strained structures, which are altered by illumination. However, such distortions seem to be practically neglected, due to small applied forces; the elastic strains in reported experiments being only at levels of 10^{-3} – 10^{-2} [3–8]. In addition, thermal disorder effects could also be neglected, since the photoinduced fluidity is conspicuous at low temperatures (≥ 220 K) [3–8]. These situations may put forward the following scenario; Urbach-edge light excites LP electrons at disordered atomic sites having smaller, local optical gaps, and then the sites athermally undergo structural changes such as chain breakages, which release local strains and cause fluidity under weak external forces. We therefore first examine what kinds of disordered structures can possess smaller optical gaps, and next how the excited sites undergo structural changes. Note that, to the author's knowledge, no computational studies have been performed on electronic excitation effects in PE-like polymers, despite of extensive works on dye-doped polymers [27,28].

2. Modeling and calculations

Substantial theoretical studies have been performed for electronic and structural properties of disordered chain/ring(-like) a-Se structures. For instance, molecular-dynamics (MD) calculations have provided valuable insights into global electro-structural evolutions [29–32]. Nevertheless, the method is inadequate to analyze elemental processes. Also, several challenging ideas trying to connect atomic structures to macroscopic viscosity have been presented [33–36], while it seems difficult to apply such approaches to electronically excited states.

Taking these backgrounds into account, we here analyze simple clusters, $H-nSe-H$ with n being an integer, using a molecular-orbital

(MO) method. The terminal H is attached to compensate dangling-bond effects, and it may also represent a connected chain. The local optical gap could be estimated from the exciton-excitation energy E_{exc} (or the HOMO-LUMO energy E_{HL}) in strained Se clusters. Specifically, we examine structure-energy correlations mainly for three clusters: i) $H-4Se-H$, which is the shortest chain possessing necessary structural factors (r , θ and φ) characterizing longer chains [37,38], and accordingly, it could typify a chain segment in a-Se. ii) A dimer consisting of $H-Se-H$ and $H-3Se-H$, which also contains four Se atoms for comparison. Disorder is likely to exist in varied inter-cluster atomic distances R . And, iii) a pair of $H-2Se-H$, in which the inter-cluster distance may be reduced by viscous motions, and the pair ultimately overcomes intercrossing. Such a process is inevitable to release knots in entangled chains.

Employed softwares were an ab initio molecular orbital package GAMESS [39] operating on a graphic platform Winmster [40], the details being described previously [37,38]. In short, a selected base function was of the $6-31+G^*$ type and the B3LYP-DFT approximation was adopted, the combination having been demonstrated to provide satisfactory results with acceptable computation times (≤ 1 day). Equilibrium shapes were obtained through the energy-optimization calculation of the total energy E_T , and the excitonic state with E_{exc} was analyzed using the time-dependent DFT routine in GAMESS.

3. Results

Fig. 2 shows E_{exc} as a function of the strain energy ΔE_T for the three clusters. At the equilibrium (X in Fig. 2, Fig. 3(a)), $H-4Se-H$ has a helical structure with $r = 2.37$ Å, $\theta = 107^\circ$ and $\varphi = 87^\circ$, which give the distance L between the far-side Se atoms at 4.9 Å and $E_{exc} = 3.27$ eV ($E_{HL} = 4.03$ eV), consistent with previous results [37,38]. In the clusters of $H-Se-H$: $H-3Se-H$ (Y in Fig. 2, Fig. 4(a)) and paired $H-2Se-H$ (Z in Fig. 2, Fig. 6(a)), the inter-cluster distances have initially been set greater than ~ 7 Å. These three systems possess E_T of -9605.886 , -9607.053 , and -9600.497 H, respectively, which are taken as references at $\Delta E_T = 0$ in Fig. 2. The slightly different E_T values, despite of the same number ($= 4$) of Se atoms, reflect structural differences including the cluster sizes and two/four H atoms. Also, E_{exc} at the equilibriums are different with the same reason, so that the absolute values of E_{exc} have little meanings when considering practical situations in a-Se.

Note that the figure plots only E_{exc} for simplicity, since the variations of E_{exc} and E_{HL} are roughly parallel, with the latter being greater

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