

Key Engineering Materials Vol.13-15 (1987) pp.501-504

EXPONENTIAL BAND TAILS AS A CONSEQUENCE OF THE GLASS TRANSITION

J.C. Dyre

IMFUF, Roskilde Universitetscenter
Postbox 260, 4000 Roskilde (Denmark)

ABSTRACT

A recently proposed theory for the glass transition is briefly reviewed. The theory predicts two different kinds of glass transitions, slow and fast. It is argued that glassy semiconductors prepared from a fast glass transition have exponential band tails of localised states.

The assumption of exponential band tails in amorphous semiconductors explains many different observations, including transient experiments [1,2], the Meyer-Neldel rule [3,4], optical properties like photoluminescence and the Urbach tail [5,6], and, possibly, the discrepancy between experimental and theoretical values of the preexponential factor in Mott's $T^{-1/4}$ -law [7, 8]. Exponential band tails are becoming a new paradigm for amorphous semiconductors, but the origin of the band tails is still not understood. Most theories predict a density of tail states which is more complicated than a simple exponential [9, 10]. Experiments, on the other hand, show that the band tail density of states is, to a high accuracy, a simple exponential function of energy [11]. Theories for amorphous semiconductor band structure usually assume an element of randomness meant to reflect the non-crystallinity, so a possible explanation for the failure of the theories is that amorphous semiconductors cannot be considered as random. After all, the formation of a non-crystalline semiconductor involves a gradual arrest of atomic motion and there seems to be no reason that this should lead to a random structure. Arguing along these lines, it has recently been suggested that the exponential band tails may originate from the semiconductor formation process itself [2,4,12,13,14]. If correct, this would be very satisfactory since exponential band tails arise in very different systems which have little in common but the fact that they are formed via some kind of quenching of thermal equilibrium. A simple theory for the glass transition is outlined below [14]. It will be argued that in some cases the glass transition leads quite naturally to exponential band tails in the glassy solid. Though the theory assumes the semiconductor is prepared via an ordinary glass transition, it is hoped that a similar theory is applicable for vapour deposited amorphous semiconductors because, even in this case, the formation process

involves an arrest of atomic motion.

Since glasses are formed from viscous liquids, a better understanding of glass structure and in particular of the band structure of glassy semiconductors must derive from an understanding of the viscous liquids. It turns out that most authors have arrived at more or less the same picture of viscous flow in highly viscous liquids [15,16,17]: since a high viscosity implies a very low diffusion constant, most molecular motion goes into vibrations. Occasionally effective displacements of the molecules do take place, however. These "flow events" must be cooperative because one molecule cannot move without having its neighbours moving too. The liquid is regarded as an ensemble of "regions", each of which spends most time vibrating in a potential energy minimum and which only quite seldomly "jumps" to another energy minimum. There is evidence in favour of this picture from computer simulations [18], and from dielectric and phosphorescence lifetime measurements [19, 20].

The dynamics of the regions is described by means of transition state theory [14,17,21]. The transition state is assumed to correspond to the high-temperature "fluid" liquid with energy E_0 [21] (henceforth energy means potential energy and a "state" is an energy minimum). The relaxation time for transitions from a state of energy E , $\tau(E)$, is given by

$$\tau(E) = \tau_0 \exp[(E_0 - E)/T] \quad (1)$$

where τ_0 is a microscopic time and $k_B = 1$. Since the "fluid" state has a structure much different from the lower lying states it is reasonable to assume that, once excited into this state, a region has forgotten which state it came from. This leads to the following master equation for the energy probability distribution, $P(E,t)$, [14]

$$\frac{\partial P(E,t)}{\partial t} = -\frac{P(E,t)}{\tau(E)} + n(E) \int_0^{E_0} \frac{P(E',t)}{\tau(E')} dE' \quad (2)$$

where τ is given by eq. (1), $n(E)$ is the normalized density of states, and the lowest region energy is zero. Because each region contains many molecules $P(E,t)$ is approximately a gaussian in thermal equilibrium. Upon cooling the gaussian is displaced towards lower energies. If t_0 is the cooling time, the equation $\tau(E) = t_0$ defines a characteristic energy, E_d , given by

$$E_d = E_0 - T \ln(t_0/\tau_0). \quad (3)$$

Regions with energy less than E_d are frozen. The glass transition takes place when, at cooling, the equilibrium gaussian meets E_d . Two different scenarios are possible [14]. Denoting the region specific heat at the glass transition by c_g , the case when $\ln(t_0/\tau_0) \gg c_g$ may be termed a slow glass transition. In this case E_d moves much faster than the gaussian as T decreases. When E_d meets the gaussian, E_d sweeps across it and freezes it, resulting in a gaussian distribution of frozen-in energies in the glass. The opposite case of a fast glass transition ($\ln(t_0/\tau_0) \ll$

EXPONENTIAL BAND TAILS

503

c_g) is characterized by a slowly moving E_d and a fast moving gaussian. Then each region jump in energy until it happens to hit an energy below the almost constant E_d . This happens with a probability proportional to the density of states, so the frozen-in distribution of energies, $P_0(E)$, is roughly speaking given by $P_0(E) \propto n(E)$ for $E < E_g$ and zero above E_g , where E_g is the equilibrium region energy at the glass transition. Since $n(E)$ is approximately exponential here, we find

$$P_0(E) = \begin{cases} T_g^{-1} \exp[(E - E_g)/T_g], & E < E_g \\ 0, & E > E_g \end{cases} \quad (4)$$

where T_g is the glass transition temperature.

According to the above theory there exist two different kinds of glass transitions, slow and fast. It will now be shown that exponential band tails arise naturally for semiconductors prepared by a fast glass transition [14]. It is assumed that the region energy, E , is a function of the density, so small densities correspond to large energies, certainly a reasonable assumption [17]. If \bar{r} denotes the average distance between atoms in a region, \bar{r} is expected to fluctuate only little and may be expanded to first order in E . Also, the average transfer integral for electron jumps between atoms in a region, \bar{t} , may be expanded to first order in \bar{r} . It is now concluded from eq. (4) that the distribution of \bar{t} 's throughout the glassy semiconductor, $p(\bar{t})$, is approximately exponential:

$$p(\bar{t}) = \exp(-\bar{t}/T_0), \quad T_0 = T_g \left. \frac{d\bar{r}}{dE} \right|_{\bar{t}} \left. \frac{d\bar{t}}{d\bar{r}} \right|_{\bar{t}} \quad (5)$$

If $n(\epsilon, \bar{t})$ denotes the tight-binding density of states, the bulk density of states, $n(\epsilon)$, is given by

$$n(\epsilon) = \int_0^{\infty} n(\epsilon, \bar{t}) p(\bar{t}) d\bar{t} \quad (6)$$

The band width of $n(\epsilon, \bar{t})$ is proportional to \bar{t} and therefore eqs. (5) and (6) imply that $n(\epsilon)$ has exponential band tails. The tail states are localised within a region while midband states probably delocalise when electron jumps between regions are allowed for.

The theory predicts gaussian band tails if the semiconductor is prepared by a slow glass transition. A careful experimental investigation of the cooling rate dependence of the band tail density of states would be most interesting.

REFERENCES:

1. J.M. Hvam and M.H. Brodsky, Phys. Rev. Lett. (1981) 46, 371.
2. J. Orenstein and M. Kastner, Phys. Rev. Lett. (1981) 46, 1421.
3. G.G. Roberts, J. Phys. C (1971) 4, 3167.

4. J.C. Dyre, *J. Phys. C* (1986) 19, 5655.
5. D.J. Dunstan and F. Boulitrop, *Phys. Rev. B* (1984) 30, 5945.
6. S. Abe and Y. Toyozawa, *J. Phys. Soc. Japan*(1981) 50, 2185.
7. M. Ortuno and M. Pollak, *Phil. Mag. B* (1983) 47, L 93.
8. N. Maloufi, A Audouard, M. Piecuch, and G. Marchal, *Phys. Rev. Lett.*(1986) 56, 2307.
9. I.M. Lifshitz, *Adv. Phys.*(1964) 13, 483.
10. B.I. Halperin and M. Lax, *Phys. Rev.* (1966) 148, 722 and *Phys. Rev.*(1967) 153, 802.
11. D. Monroe and M.A. Kastner, *Phys. Rev. B* (1986) 33, 8881.
12. M. Roberts and D.J. Dunstan, *J. Phys. C* (1985) 18, 5429.
13. Y. Bar-Yam, D. Adler, and J.D. Joannopoulos, *Phys. Rev. Lett.* (1986) 57, 467.
14. J.C. Dyre, preprint (1986).
15. G. Adam and J.H. Gibbs, *J. Chem. Phys.* (1965) 43, 139.
16. M. Goldstein, *J. Chem. Phys.* (1969) 51, 3728.
17. S.A. Brawer, *J. Chem. Phys.* (1984) 81, 954.
18. S. Brawer, "Relaxation in Viscous Liquids and Glasses" (American Ceramic Society, Columbus, Ohio, 1985).
19. M.S. Beevers, J. Crossley, D.C. Garrington, and G. Williams, *Faraday Symp. Chem. Soc.* (1977) 11, 38.
20. J. Leduc and A.H. Kalantar, *J. Chem. Phys.*(1980) 73, 5330.
21. M. Goldstein, *Faraday Symp. Chem. Soc.* (1972) 6, 7.

Amorphous Metals and Semiconductors

10.4028/www.scientific.net/KEM.13-15

Exponential Band Tails as a Consequence of the Glass Transition

10.4028/www.scientific.net/KEM.13-15.501