Random walk approach for the proper estimation of density of defect states in amorphous chalcogenides

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Abstract

Recently, the present authors proposed a correlated barrier hopping model for bipolarons based on continuous-time random-walk approximation to explain ac conductivity in a-As2Se3 and estimated the density of defect states based on this approach. It was observed that the density of defect states deduced from this approach is less than as deduced from correlated barrier hopping based on pair approximation and are consistent with the estimated density of defect states from other studies, namely, light-induced electron spin resonance and drift mobility. Now, this approach is extended to the single- and bi-polaron contribution to ac conductivity and apply to the experimental data of a-Se and a-As2Se3 + 0.5 at.% Ag. The present approach explains the single- as well as bi-polaron contribution to ac conductivity and the deduced density of defect states is less than that deduced from correlated barrier hopping based on pair approximation.

1. Introduction

Correlated barrier hopping (CBH) of charge carriers is well established to induce ac loss in amorphous chalcogenides. CBH of bipolarons (two electrons hopping between charged defects D+ and D-) as proposed by Elliott [1,2] for weak temperature dependence, and for strong temperature dependence at higher temperatures, the CBH of single polarons (electrons hopping between neutral and charged defects, D0 and D+, and holes hopping between D0 and D–) as proposed by Shimakawa [3] are able to interpret the temperature and frequency dependence of ac conductivity in amorphous chalcogenides to a large extent. These theories are based on the ‘pair approximation’ (PA), in which the carriers are confined to a pair of centers. On fitting CBH for single- and bi-polarons to the experimental data, although the fitting is fairly good, however, deduced density of charged defects (4 × 1018–4 × 1019 cm–3) [3] is fairly large and not consistent with that (1016–5 × 1017 cm–3) of other estimation techniques, e.g., LESR and drift mobility. As charged defects may dominate ac conductivity, LESR, drift mobility, etc., the estimated density of defect states should be same irrespective of the method of measurements. Also, as the carriers are not confined to a pair of centers at low frequencies, PA may not be valid at low frequencies. Since, PA treats atomic or molecular like dipoles, as treated in dipolar materials, PA cannot predict finite conductivity at zero frequency.

The continuous-time random-walk (CTRW) approximation [4,5] can be an alternative method to explain ac losses in disordered materials. This approximation considers the random hopping of carri-
ers and does not consider the confinement of charge carriers to a pair of centers. This theory, therefore, seems to be more realistic than PA approach. In order to overcome the above mentioned shortcomings of CBH based on PA, we proposed CBH based on CTRW approximation for bipolaron contribution to ac conductivity [6] and it was shown that the difference in the estimation of density of defect states arises from the underestimation of the effective ‘dipole’ length and, thus, resulting in overestimation of density of charged defects.

We have already estimated density of charged defects, consistent with LESR and drift mobility, by using CBH based on CTRW for bipolaron contribution for a-As$_2$Se$_3$ [6] and in this paper, we report the estimation of proper density of defect states for the case of both single- and bi-polarons. As, at higher temperatures, single polaron contribution becomes more prominent, it is important to apply the CBH based on CTRW approach to single polaron contribution. We have first developed the CBH based on CTRW approximation for single polaron contribution in the present work and then applied it to estimate the density of defect states for a-Se. Also, to observe the effect of impurities, we have evaluated the density of defect states of a-As$_2$Se$_3$ + 0.5 at.% Ag. The estimated density of defect states is found to be less than those estimated from CBH based on PA and the fitting to the experimental data is also observed to be fairly in agreement.

2. Theory

Following Elliott [1,2], the bi-polaron contribution of ac conductivity as derived from CBH based on PA with random distribution of centers can be written as

\[ \sigma_{ac} = \frac{n \pi^2 N N_p \omega \varepsilon_0}{6} \times \left[ \frac{n e^2}{\pi \varepsilon_0} \left( \frac{1}{W_M - kT \ln(1/\omega \tau_0)} \right) \right]^6, \]  

(1)

where \( N \) is the number of sites, \( N_p \) is the number of carriers and are estimated by fitting the above equation to the experimental data. \( W_M \) is the maximum barrier height over which the carriers must hop \( (W_M \approx B \text{ (optical band gap)} [2]) \) and \( n = 1 \) for single polaron and \( n = 2 \) for bipolaron contribution to ac conductivity. The single- and bi-polaron hopping processes are shown in Fig. 1(a).

This approach was able to explain many features at relatively low temperatures; however, it could not predict the strong temperature dependence of ac conductivity which is observed at higher temperatures in most of the chalcogenide semiconductors. The strong temperature dependence at higher temperatures has been interpreted in terms of ‘single polarons’ by Shimakawa [3]. According to Shimakawa, at higher temperatures, density of neutral defects, \( D^0 \), generated by the reverse reaction of \( 2D^0 \rightarrow D^+ + D^- \) are more important and the contribution of single polarons exceeds that of bi-polarons, and, the number of \( D^0 \), \( N_0 \), as generated by the reverse reaction can be given as

\[ N_0 = 2[D^0] = N_p \exp \left( \frac{-U_{eff}}{2kT} \right). \]  

(2)

\( U_{eff} \) is the effective correlation energy and is shown in Fig. 1(b) along with the thermal energies associated with defect states. Half of the \( D^0 \)s created are assumed to contribute to the relaxation between \( D^0 \) and \( D^- \) (process II in Fig. 1) and the other half to relaxation between \( D^0 \) and \( D^+ \) (process III in Fig.
1). The factor $N_{N_p}$ (of Eq. (1)) for single polaron contribution can, thus, be expressed as

$$N_{N_p} = N^{-} \frac{N_0}{2} = \frac{N_T^2}{4} \exp\left[\frac{-U_{\text{eff}}}{2kT}\right] \quad \text{(for process II)}$$

and

$$= N^{+} \frac{N_0}{2} = \frac{N_T^2}{4} \exp\left[\frac{-U_{\text{eff}}}{2kT}\right] \quad \text{(for process III)}.$$  \hspace{1cm} (3)

Thus, the total ac conductivity arising from the combined mechanism of single and bi-polaron hopping can be written as

$$\sigma_{\text{ac}(T)} = \sigma_{\text{ac}(b)} + \sigma_{\text{ac}(sh)} + \sigma_{\text{ac}(sc)},$$  \hspace{1cm} (4)

where $\sigma_{b}$ represents the bi-polaron contribution (process I), and $\sigma_{sh}$ and $\sigma_{sc}$ represent the single polaron contributions (process II and process III) respectively. A large temperature dependence is contributed by the second and third term of Eq. (4) due to a smaller $W_{\text{eff}}$ as compared to the bipolaron contribution and also due to an increasing number of thermally activated pairs as given by Eq. (3).

Next, we consider the continuous time random walk (CTRW) approximation. This approximation for the explanation of ac loss in disordered materials was first proposed by Scher and Lax [4] and a more simplified approach was given by Dyre [5]. The CTRW approximation takes into account the random hopping of the charge carriers over random hopping distances and jump frequencies in the disordered solid. This model seems to be more realistic than PA approximation as it is able to explain the ac loss over a wide frequency range and the dc limit can also be explained.

The dc hopping conductivity can be given as

$$\sigma_{\text{dc}} = \frac{n_0(eR_C)^2}{6kT} \Gamma,$$  \hspace{1cm} (5)

where $n_0$ is the number of hopping carriers, and $N_T/2$ for bipolaron contribution, and for single polaron contribution $= N_T/2 \exp[-U_{\text{eff}}/2kT]$, and, $\Gamma$ is the hopping rate and is given as $\Gamma = 1/\tau_C$, where $\tau_C$ is the hopping relaxation time at the critical percolation length, $R_C$. The critical percolation length, $R_C$, which will connect the percolation path can be written as $R_C = [2.7 \times 3/(N_T/2)^2]^{1/3}$ [7]. It must be noted here, that, since dc hopping is a percolation problem, $R_C$ cannot be considered as the average hopping distance.

Following Dyre [5], the real part of ac conductivity is written as

$$\text{Re} \left[ \sigma(\omega) \right] = \sigma_{\text{dc}} \left[ \frac{\omega \tau_C \arctan(\omega \tau_C)}{[\ln(1 + (\omega \tau_C)^2)^2 + [\arctan(\omega \tau_C)]^2]} \right],$$  \hspace{1cm} (6)

where $\omega$ is the angular frequency of the applied field. As can be seen from Eq. (6), ac conductivity and dc conductivity are closely related.

3. Application to experiment

In order to estimate the density of defect states and compare them with those estimated from CBH based on PA, we apply the CBH based on CTRW approximation to the experimental data of a-As$_2$Se$_3$ (from Ref. [6]), a-Se, and also in order to observe the effect of alloying with impurities on the ac conductivity, to the experimental data of a-As$_2$Se$_3 + 0.5\%$ Ag. The experimental data ($\sigma_T = \sigma_{\text{dc}} + \sigma_{\text{ac}}$; filled circles) and the calculated curves from CBH based CTRW (dotted for bi-polaron contribution, dash-dotted for single-polaron contribution and the solid curve represents the total conductivity ($= \sigma(b) + \sigma(s)$) as a function of temperature at various frequencies are shown in Figs. 2–4 for a-As$_2$Se$_3$, a-Se and a-As$_2$Se$_3 + 0.5$ at.% Ag, respectively. As can be seen from the figures, CBH based on CTRW is fairly able to explain the experimental data to a large extent. The departure from the bipolaron behavior at higher temperatures is taken ‘care of’ by the single polaron contribution. The values of various parameters, the maximum barrier height, $W_M$, the energy bound states, $W_b$, and the effective negative correlation energy, $U_{\text{eff}}$, are shown in Table 1. Fitting the data to Eq. (6), we were able to deduce the density of defect states $N_T$, and the deduced values along with the estimated values from CBH based on PA [3] are shown in Table 1. As can be clearly seen from the table, the density of defect states as deduced from CBH based on CTRW are two to three orders less than as deduced from CBH based on PA.
Fig. 2. Temperature dependence of $\sigma_{ac}$ as a function of inverse temperature at various frequencies for a-As$_2$Se$_3$. Total conductivity ($= \sigma_T + \sigma_{dc}$) and $\sigma_{dc}$ are the experimentally obtained data (from Kitao [8]). The dashed (-----) and the dashed dotted (- ---) line represents the single and bipolaron contributions to ac conductivity, respectively, as calculated from CBH based on CTRW approximation. The total conductivity is shown by the solid line (———). In the case of the impurity alloying, i.e., As$_2$Se$_3$ + 0.5 at.% Ag, a strong temperature dependence has been observed by Kitao et al. [10] as is shown in Fig. 4. Such a large temperature dependence has not been observed in the case of amorphous As$_2$Se$_3$ and we were able to explain the data on the basis of bipolaron contribution alone [6]. In the case of As$_2$Se$_3$, the effective correlation energy, $U_{eff}$, may be larger than that for other chalcogenide systems, and thus, the density of D$^0$s, $N_0$, is much smaller and hence, single polaron contribution does not dominate and a weak temperature dependence is observed. Also, it

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_M$ (eV)</th>
<th>$W_I$ (eV)</th>
<th>$U_{eff}$ (eV)</th>
<th>$N_T$ (cm$^{-3}$) CBH based on CTRW</th>
<th>$N_T$ (cm$^{-3}$) CBH based on PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$Se$_3$</td>
<td>1.80</td>
<td>-</td>
<td>-</td>
<td>$2.0 \times 10^{17}$</td>
<td>$2.4 \times 10^{19}$</td>
</tr>
<tr>
<td>Se</td>
<td>2.00</td>
<td>0.63</td>
<td>0.32</td>
<td>$1.0 \times 10^{18}$</td>
<td>$2.4 \times 10^{19}$</td>
</tr>
<tr>
<td>As$_2$Se$_3$ + 0.5 at.% Ag</td>
<td>1.85</td>
<td>0.50</td>
<td>0.33</td>
<td>$5.0 \times 10^{17}$</td>
<td>$4.2 \times 10^{19}$</td>
</tr>
</tbody>
</table>
can be seen from the table that the addition of Ag introduces more defects in As$_2$Se$_3$.

4. Conclusion

CBH based on CTRW approximation for single- and bi-polaron contribution to ac conductivity has been developed and has been used to estimate the density of defect states. This approach has been applied to the experimental data for a-As$_2$Se$_3$, a-Se and a-As$_2$Se$_3$ + 0.5 at.% Ag. The estimated density of defect states is found to be lower than that of CBH based on PA. Thus, the short coming of pair approximation, i.e., overestimation of density of charged defects, $N_T$, has been overcome using the present approach. The role of impurities has been explained by considering the case of a-As$_2$Se$_3$ + 0.5 at.% Ag. It is observed that addition of Ag introduces more defects in a-As$_2$Se$_3$. It can thus be concluded that CBH induces ac loss in amorphous chalcogenides. Also, it can be concluded that ac conductivity is a good and proper method for the estimation of density of defect charged states and we have shown that by applying it to certain amorphous chalcogenides and found the explanation fairly in agreement.

References