Effect of valence band and conduction band discontinuities on the electronic structures and conduction properties of copolymers of Type-I

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Received 27 June 2006; revised 4 December 2006

The effect of change in the ratio of conduction band discontinuity to the valence band discontinuity \( \frac{\Delta E_c}{\Delta E_v} \) on the electronic structures and conduction properties of model copolymers \( (A_mB_n)_x \), belonging to the class of Type-I quasi-one-dimensional superlattices are reported. Six different systems of copolymers \( (A_mB_n)_x \), differing in respect of the ratio \( \frac{\Delta E_c}{\Delta E_v} \), have been modelled using the model band structure of constituent homopolymers \( (A)_x \) and \( (B)_x \). For each of these systems of copolymers the electronic density of states of the various periodic and aperiodic copolymer chains have been determined on the basis of negative factor counting method in tight binding approximation. The trends obtained in the electronic structures and conduction properties of these copolymers as a function of the ratio \( \frac{\Delta E_c}{\Delta E_v} \) are useful guidelines for designing copolymers with desired electronic and conduction properties.

Molecular designing of novel polymers continues to be a major challenge in the field of electrically conducting polymers. To be successful in this designing, one needs to have a complete understanding of the relationship between the chemical structure of the polymer and its electronic properties which determine its conduction properties. Of the various strategies presently used for designing, the strategy of copolymerisation is very exciting and promising and has been used to design copolymers with desired electronic and conduction properties.

Methodology

The electronic density of states (DOS) of both periodic and aperiodic copolymer chains \( (A_mB_n)_x \), were determined using a simple negative factor counting method based on Dean's negative eigenvalue theorem. This method was used to compute the electronic DOS by finding the number of eigenvalues of a tridiagonal tight-binding (Hückel) secular determinant (Eq. 1), of a copolymer chain, which are smaller than a given trial energy, \( \lambda \), by using the following recursion relations. The later expressions were obtained by transforming the tridiagonal Hückel...
determinant to a didiagonal one by applying successive Gaussian elimination. Here \( \alpha_i \) and \( \beta_i \) denote the onsite and hoping parameters in the first neighbour interaction approximation. In the present calculations of the DOS, the \( \alpha \) and \( \beta \) values for both the valence and the conduction bands of \((A)_x\) and \((B)_x\) in all the six different systems were obtained from their model band structures (Fig. 1). In all of these calculations, we have consistently used a chain length of 300 units and an energy grid of 0.02 eV.

\[
\begin{pmatrix}
\alpha_1 - \lambda & \beta_2 & 0 & \ldots & 0 \\
\beta_2 & \alpha_2 - \lambda & \beta_3 & \ldots & 0 \\
0 & \beta_3 & \alpha_3 - \lambda & \beta_4 & 0 \\
0 & 0 & \beta_4 & \ldots & \beta_N \\
0 & 0 & 0 & \ldots & \alpha_N - \lambda
\end{pmatrix} = 0
\]  

\( \varepsilon_1(\lambda) = \alpha_1 - \lambda \) \hfill \ldots (2)

\( \varepsilon_i(\lambda) = (\alpha_i - \lambda) - \frac{\beta_i^2}{\varepsilon_{i-1}(\lambda)} \); \( i = 2, 3, \ldots, N \) \hfill \ldots (3)

Results and discussion

Electronic properties of the copolymers

In the present study, both periodic and aperiodic copolymers \((A_mB_n)_x\) have been modelled by coupling ‘m’ units of ‘A’ and ‘n’ units of ‘B’ blockwise periodically and aperiodically in the six different systems (System 1 to System 6). The model band structures of homopolymers \((A)_x\) and \((B)_x\), constituting these systems of copolymers \((A_mB_n)_x\), belonging to the class of Type-I are shown in Fig.1. It is evident from Fig. 1 that both the homopolymers, \((A)_x\) and \((B)_x\), constituting these six systems of copolymers have the same values of \( E_g \) (Band gap) in all of these six systems of copolymers. Also, the values of both the valence band width and the conduction band width of both the homopolymers \((A)_x\) and \((B)_x\) remain same in all the six systems of copolymers. On the other hand, these systems of copolymers differ from one another in respect of the band alignments of both valence band and conduction band of homopolymer \((A)_x\). Consequently, the values of both the conduction band discontinuity \( \Delta E_c \) and the valence band discontinuity \( \Delta E_v \) and hence their ratio \( \Delta E_c/\Delta E_v \) is different in each of these six systems of copolymers.

Fig. 1—Model band structure of homopolymers \((A)_x\) and \((B)_x\) in six different systems of copolymers \((A_mB_n)_x\) belonging to the class of Type-I quasi-one-dimensional superlattices. All values in (eV).
Thus, on moving from system 1 to system 6, both the valence and conduction band discontinuities and also their ratio $\Delta E_c/\Delta E_v$ increase (Table 1).

In the present study each of these six systems has been classified systematically in the following three categories.

**Category 1**: $(AB_n)_x$; in this category of copolymers the block size $m$ of the first component is kept constant ($m=1$) while the block size $n$ of the component B is varied along a copolymer chain.

**Category 2**: $(A_mB)_x$; here the block size $n$ of the component B is kept constant ($n=1$) and the block size $m$ of the component A is varied.

**Category 3**: $(A_mB_n)_x$; this includes copolymers in which the block sizes $m$ and $n$ of both the components are varied keeping their ratio $m/n$ constant.

The calculated electronic properties ionization potential (IP), electron affinity (EA) and band-gap ($E_g$) of both the periodic and aperiodic copolymer chains for all the six systems obtained from their corresponding DOS curves are given in Table 2.

**Periodic copolymers**

It is evident from Table 2 that in all the three categories of periodic copolymers, on going from System 1 to System 6, the value of ionization potential (IP) of a copolymer chain increases with an increase in the ratio $\Delta E_c/\Delta E_v$, Fig. 2 (a). This indicates that the ability of these copolymers to show extrinsic conductivity through oxidative or p-doping decreases, with an increase in $\Delta E_c/\Delta E_v$. Thus, the copolymers having smaller magnitude of the ratio $\Delta E_c/\Delta E_v$ are expected to be better candidates for p-doping.

The electron affinity (EA) values for all the three categories of periodic copolymers also increase with the ratio $\Delta E_c/\Delta E_v$, Fig. 2 (b). It, therefore, implies that an increase in the ratio $\Delta E_c/\Delta E_v$ makes these copolymers, better candidates for reductive or n-doping. These copolymers are therefore expected to undergo n-doping even with relatively mild reducing agents.

Since the increase in the EA decreases the band gap ($E_g$) while an increase in IP increases it, the observed change in $E_g$ values with an increase in $\Delta E_c/\Delta E_v$ ratio will be depend upon the relative increase in the IP and EA values. Thus as is evident
<table>
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<tr>
<th>Copolymers ((\mathbb{A}_n\mathbb{B})_x)</th>
<th>System 1</th>
<th>System 2</th>
<th>System 3</th>
<th>System 4</th>
<th>System 5</th>
<th>System 6</th>
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<tr>
<td></td>
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<td>EA</td>
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<td></td>
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<td>4.58</td>
<td>3.56</td>
<td>8.26</td>
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<td>3.06</td>
<td>8.02</td>
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<td>8.00</td>
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from Fig. 2 (c) that the band gap value increases with increase in \( \Delta E_c/\Delta E_v \) upto system 4 and then decreases from system 4 to system 6 for all types of copolymers. It, therefore, means that upto system 4, the increase in IP values is much more than the corresponding increase in EA values whereas from system 4 to system 6, the increase in EA values is much more pronounced than the corresponding increase in IP values.

Thus, a copolymer chain is expected always to become a better candidate for reductive (n-) doping and a poor candidate for oxidative (p-) doping with an increase in \( \Delta E_c/\Delta E_v \) ratio but its tendency to show intrinsic conductivity may increase or decrease depending upon the relative changes in IP and EA values. It may also be noted from Table 2 that in contrast to the copolymers of \((A_mB)_x\) category, in the case of copolymers of \((Ab_n)_x\) and \((A_mB_n)_x\) categories stagnation in electronic properties is reached relatively faster.

**Aperiodic copolymers**

Unlike periodic copolymers, the trends in electronic properties of aperiodic copolymers are different for the three different categories of copolymers. In the case of \((AB_n)_x\) and \((A_mB_n)_x\) categories of aperiodic copolymers, the values of ionization potential (IP), electron affinity (EA) and the band gap (Eg) remain same with an increase in the ratio \( \Delta E_c/\Delta E_v \) from system 1 to system 6. It means that for these aperiodic copolymers the values of IP, EA and Eg are already at saturation level. Here, the copolymer chain \((AB)_x\) is an exception, for which the values of both IP and Eg increase initially from system 1 to system 2 but remains same from system 2 to system 6.

On the other hand, for aperiodic copolymers of the type \((A_mB)_x\), the IP values are generally found to increase with the ratio \( \Delta E_c/\Delta E_v \) while corresponding EA values remain constant from system 1 to system 4, followed by an increase from system 4 to system 6. As a result, the Eg values of these copolymers increase initially from system 1 to system 3 and then decrease from system 4 to system 6. Therefore, for aperiodic copolymers of \((A_mB)_x\) category, the trends in Eg values resemble the trends in Eg values of corresponding periodic copolymers.

It may further be noted from Fig. 3, that aperiodic copolymer \((A_2B)_x\) is an exception in this category of copolymers, because the values of electronic properties instead of showing variation remains constant with the ratio \( \Delta E_c/\Delta E_v \).

**DOS distributions**

The DOS distribution curves for both the valence and the conduction bands of both the periodic and aperiodic copolymers \((A_2B_2)_x\), of system 1, are shown in Fig. 4. The DOS curves of periodic copolymer consist of relatively narrower and well separated peaks while this feature of the DOS curves of aperiodic copolymer is missing in the DOS curves of periodic copolymer and consists of relatively broader regions of allowed energy states. Consequently the band gap for aperiodic copolymer is less than that for the corresponding periodic copolymer and hence leads to
a faster saturation in electronic properties for aperiodic copolymers. Such features have also been observed in recent studies on both model and real copolymers\textsuperscript{12-13} and also in various copolymers in the present study.

We have investigated the effect of the change in the ratio $\Delta E_c/\Delta E_v$ on the electronic structures and conduction properties of model copolymers $(A_mB_n)_x$ of Type-I. The results of our investigation shows that a copolymer chain is expected always to become a better candidate for reductive (n-) doping and a poor candidate for oxidative (p-) doping with an increase in $\Delta E_c/\Delta E_v$ ratio but its tendency to show intrinsic conductivity may increase or decrease depending upon the relative changes in IP and EA values. These trends are very useful guidelines for designing copolymers with desired electronic and conduction properties.

References