Comments on the Meyer–Neldel rule in amorphous semiconductors

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Abstract. In this paper, we show that the Meyer–Neldel rule can be satisfactorily explained by the temperature dependence of the Fermi level. We argue that the universality of the Meyer–Neldel rule can be explained by the fact that the dangling bond is the dominant defect in amorphous silicon.

Keywords. Meyer–Neldel rule; dc conductivity; amorphous semiconductors.

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1. Introduction

The Meyer–Neldel rule in amorphous semiconductors relates the dc conductivity prefactor $\sigma_0$ to the activation energy $\Delta E$ through the relation

$$\log \sigma_0 = \log \sigma_{00} + \frac{\Delta E}{E_0}. \quad (1)$$

In a-Si:H, the Fermi level position can be changed by doping and the Meyer-Neldel relation can be demonstrated quite vividly (Carlson and Wronski 1979). The Meyer–Neldel relation has been attributed at various times to (a) the presence of heterogeneities (Fritzsche and Taniellian 1981), (b) the temperature dependence of the Fermi-level (Beyer and Overhof 1983) and (c) to the temperature dependence of the mobility edge (Spear et al 1983). In particular, it has been very difficult to account for large values of $\sigma_0$ ($\sim 10^7$–$10^8 \, \Omega^{-1} \, \text{cm}^{-1}$) where the dc conductivity $\sigma$ is given by

$$\sigma = \sigma_0 \exp - \left( \frac{\Delta E}{kT} \right). \quad (2)$$

It has recently been shown that the temperature dependence of the mobility edge is not marked in a-Si and so cannot account for the Meyer–Neldel rule (Bapat et al 1987; Mott 1987). We would like to emphasize that (1) is not to be interpreted in a strict mathematical sense but only as an equation emphasizing a trend. If we plot $\log \sigma_0$ vs $\Delta E$ for different amorphous semiconductors (1) is satisfied for $15 \, \text{eV} < E_0 < 30 \, \text{eV}$. In this paper we argue that the Meyer–Neldel rule can be accounted for by the temperature dependence of the Fermi-level and give a simple chemical argument to account for the universality of this relationship. In this paper we emphasize results relevant to a-Si:H alloys. We believe these arguments are also valid for other tetrahedrally bonded amorphous semiconductors.
2. Discussion

It is known for a-Si that doping affects the distributions of defect states (DOS) in the gap (Street et al. 1981; Lang et al. 1982). This can be easily understood from the following argument. The gap states can be thought of as arising from the bonding and antibonding states of weak bonds. If we attempt to fill the antibonding states (bonding states) with two electrons (2 holes), it is easy to see that the bond order tends to zero and it is energetically more favourable to have a pair of dangling bonds than occupied antibonding states (empty bonding states). In a-Si (and may be in most amorphous semiconductors), these defects tend to pile up near the middle of the gap thereby reducing the number of states near the fermi-level $E_F$. Thus, in the presence of defects and impurities, the DOS goes through a maximum near the midgap and decreases in the vicinity of $E_F$. This situation is quite different from that in crystals and we will return to this point later. When we attempt to move the Fermi level of a $n$-type (p type) a-Si sample by doping with group V (group III) impurities, the Fermi-level finds its equilibrium position in a pseudo local minimum of the DOS (Street 19887. The states removed from the vicinity of $E_F$ to create that minimum appear as dangling bonds near the midgap. This is clearly not the situation when we counterdope the specimen to change the conductivity type. For instance, if we dope with boron a nominally undoped sample ($n$ type) we produce dangling bonds near the midgap, the Fermi-level now moves through this peak in the density of states. Experimental confirmation of this peak exists in DLTS and luminescence measurements (Street et al. 1981, Lang et al. 1982). In such a case, we easily see that the temperature dependence of $E_F$ is large as it will be driven towards the minimum in the DOS when we increase the temperature. If $E_F$ changes linearly or pseudolinearly with temperature moving away from the midgap at elevated temperatures towards the minima in the DOS, then this will give rise to an enhanced conductivity prefactor in (1) and account for the large value of $\sigma_0$. Experimental confirmation of this result appears in the values of $\sigma_0$ obtained for virgin and electron irradiated samples (Premachandran et al. 1984). Electron irradiation gives rise to point defects near the midgap in a-Si. These defects can be annealed out by heating to 150°C. In these experiments both $dE_F/dT$ and $\sigma_0$ were independently monitored. After electron irradiation the value of $dE_F/dT$ was found to remain unaltered whereas that of $\sigma_0$ increases. This increase in $\sigma_0$ is related to a change in the value of $dE_F/dT$ before and after irradiation (Premachandran et al. 1984). In these experiments on some samples $dE_F/dT$ was even found to change sign after irradiation indicating the presence of a maxima in the density of states near the midgap after electron irradiation. The presence of this maxima in the density of states near midgap also shows up in space charge limited currents where at small voltages the current increases rapidly with applied voltage as the quasi fermi-level $E_{Fn}$ is swept across to the minima in the density of states (Bhattacharya and Narasimhan 1984). We hence conclude that the temperature dependence of $E_F$ is in fact responsible for the large values of $\sigma_0$. Beyer and Overlof (1983) come to a similar conclusion in their experiments using lithium doped samples.

In c-Si, points defects are easily generated by radiation damage. These defects, in some sense, are also dangling bonds with the difference that the energy level of the defect is dependent on the impurity – O, P, B, C etc. The defect varies in energy from $E_c - 0.2$ eV to $E_c - 1.0$ eV depending on the nature of the complex with the impurity (Watkins et al. 1979). Such complexes appear to be unimportant in a-Si. Here, the
dominant defect seems to be the dangling bond near midgap. This accounts for the fact that the Meyer–Neldel rule relates $\sigma_0$ to $\Delta E$ as the temperature dependence of $E_F$ depends on the DOS distribution in the vicinity of $E_F$ which in turn depends on the position of $E_F$ in the gap. The fact that the Meyer–Neldel rule is seen in amorphous semiconductors suggests that defects behave similarly in all amorphous semiconductors (and to that extent are different from and simpler than defects in crystalline semiconductors. This also accounts for the universality of the Meyer–Neldel rule in amorphous semiconductors.

References

Bhattacharya E and Narasimhan K L 1984 (unpublished)
Carlson D E and Wronski C R 1979 in Amorphous semiconductors (ed.) M H Brodsky (New York: Springer), p. 287
Mott N F 1987 J. Phys. C21 3075
Street R A 1988 – Private Communication