Electronic and optical properties of hydrogenated microcrystalline silicon: review

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Current understanding of electronic transport and optical properties of hydrogenated microcrystalline Si (μc-Si:H) prepared by plasma enhanced chemical vapor deposition are briefly reviewed. Research to date shows that the effective-medium approximation is a useful model in understanding the physical properties of μc-Si:H.

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1. Introduction

Microcrystalline Si films (μc-Si:H) prepared by chemical vapor deposition appear as a promising material for thin-film devices such as solar cells, thin-film transistors, and sensors. Understanding the electronic transport and optical properties of μc-Si:H is very important for improving such device properties. However, as schematically shown in Fig. 1, the μc-Si:H structure is expected to be characterized by “crystalline grain clusters” (region A) which consist of crystalline grains of size about 20 nm, surrounded by “disordered zones” (region B) [1,2]. Region A forms columnar clusters of much larger dimensions extending perpendicular to the substrate. Although the influences of the grain size and crystalline volume fraction on the electronic transport have been discussed previously in the literature, the details of their quantitative interpretation are still not clear [1–8].

A percolation path for electronic transport in μc-Si:H films has been suggested [3] and three-dimensional conductance network calculations (computer simulations) for the conductivity σ, and Hall mobility, μ_H, show the existence of a critical threshold for such a percolation path [9]. It is predicted that an effective medium approximation (EMA) [10] is useful for explaining the transport and optical properties of μc-Si:H films that depend strongly on the crystalline volume fraction. In the present paper, the current understanding of electronic and optical properties of μc-Si:H films is briefly reviewed using the ideas of the EMA model in which, for simplicity, a random mixture of particles (regions A and B) is assumed [11,12].

2. Effective medium approximation

It is instructive to briefly introduce the EMA. EMA has been widely used to explain the observed physical properties of a wide range of materials that are structurally or compositionally heterogeneous, there are numerous examples in the literature. The EMA predicts the total network conductance σ_n for composite materials in D dimensions is given by [10]

\[
\left\langle \frac{\sigma - \sigma_m}{\sigma + (D-1)\sigma_m} \right\rangle = 0
\]

where σ is a random variable of conductivity, and the triangular brackets represent spatial averaging. Assuming that a random mixture of particles of two different conductivities, e.g. a volume fraction C, has conductivity of σ_0 and the remainder (1−C) has conductivity of σ_1 substantially less than σ_0, simple analytical expressions of d.c. conductivity and Hall mobility as a function of C, have been derived (see the pioneering works by Kirkpatrick [10] and Cohen and Jortner [13] and the references therein). EMA has been also extended to calculate the a.c. conductivity in which case σ in Equation 1 becomes a complex conductivity (σ = σ_r + iσ_i) [14]. The complex permittivity with real and imaginary parts ε_r and ε_i is closely related to the complex conductivity σ by

\[
\varepsilon^* = \varepsilon_1 - i\varepsilon_2 = \sigma_2/\omega - i\sigma_1/\omega_2
\]

The optical absorption coefficient α(ω) can be also calculated using

\[
\alpha(\omega) = \omega\varepsilon_2/({\varepsilon_0}cn) = \sigma_1(\omega)/({\varepsilon_0}cn)
\]

where ε_0 is the absolute permittivity, c is the speed of light, n the refractive index, and n^2 is the relative permittivity (ε_r/ε_0).

3. Application of EMA to the experimental data

Solid circles in Fig. 2 show the room-temperature conductivity data as a function of crystalline volume
fraction, $X_c$, for a series of undoped $\mu$-c-Si:H [3]. Shimakawa [11] has applied the EMA to the experimental data and the result of the EMA is shown by the solid line, where $\sigma_1 = 3 \times 10^{-8} \Omega^{-1} \text{cm}^{-1} (X_c = 0)$ and $\sigma_0 = 3 \times 10^{-2} \Omega^{-1} \text{cm}^{-1} (X_c = 1)$ were used with $D = 3$. The experimental data do not fit the solid line very closely, which may be attributed to variations in the grain size and shape. If we follow the solid line, the percolation threshold appears at $X_c = 0.33$, which agrees very well with $X_c = 0.32$ based on computer simulation [9].

Solid circles in Fig. 3 show the room-temperature Hall mobility data for undoped $\mu$-c-Si:H as a function of volume fraction of crystalline Si [15]. Shimakawa [11, 12] has tried to confirm the Cohen and Jortner EMA approach [13] and the solid line shows the calculated result with $\mu_1 = 0.2 (X_c = 0)$ and $\mu_0 = 2 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} (X_c = 1)$. Note, however, that $\mu_1 = 0.2$ used here is not the true Hall mobility of the amorphous state ($X_c = 0$), because of the well-known anomaly of the Hall effect in hydrogenated amorphous silicon (a-Si:H) [16]. The fitting of the calculation to the experimental data is reasonably good and the percolation threshold is shown to exist at $X_c = 0.33$ [11]. The small Hall mobility ($\sim 2 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) even at $X_c = 1.0$ is about three orders of magnitude smaller than that for single-crystalline Si [17], which is probably due to the complicated structure of $\mu$-c-Si:H. As already shown in Fig. 1, the grain boundaries (between region A) dominate the transport properties and hence the mobility of $\mu$-c-Si:H films is reduced significantly; each Si crystallite wears thin “cloths” of grain boundary.

It is useful to consider the effect of crystallite size on the Hall mobility. In earlier studies [3, 5, 17], the Hall mobility with the same $X_c$ has been suggested to increase linearly with the average crystallite size $\delta$. This has been explained by the grain-boundary trapping model, in which the thermionic emission current is taken into account. However, as is apparent from Fig. 4, experimental Hall mobility data are shown to depend on the crystallite size as $\delta^\gamma$ with $\gamma \approx 0.3$ [11, 12]. This sublinear dependence of $\mu_H$ has been explained by the following argument [12]. At the same $X_c$ the area of a disordered zone (DZ) (and hence the number of localized states in region B) can be regarded to be proportional to the surface-to-volume ratio $R_{SV}$. Since $\mu_H$ is expected to be inversely proportional to the area of DZs, we get $\mu_H \propto R_{SV}^{-\gamma}$. As $R_{SV}$ is proportional to $\delta^\alpha/\delta^\beta$ where $\alpha = 2.0$ and $\beta = 3.0$ in Euclidean space whereas $\alpha < 2$ and $\beta < 3.0$ in fractal space. The relation $\mu_H \propto \delta^\gamma$ requires $\gamma = \beta - \alpha$. In the case of Euclidean space, we get $\gamma = 1$. This can be easily understood as follows. Imagine a cubic length $\delta = L$ in Euclidean space. The total surface area for this cubic is $6L^2$. When it is divided into 8 parts, i.e., $\delta = L/2$, the total surface area is $12L^2$. The total surface (grain boundary) is thus expected to be inversely proportional to $\delta$, when the volume is kept the same $L^3$. However, if we consider $\alpha$ and $\beta$ in the fractal