Percolation-controlled electronic properties in microcrystalline silicon: effective medium approach

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Abstract
Electronic transport and optical properties of microcrystalline Si prepared by plasma enhanced chemical vapor deposition are discussed in terms of effective medium approximation (EMA). The electrical conductivity and the Hall mobility as a function of volume fraction of crystalline are replicated well by the EMA calculation with a percolation threshold at 33% crystalline volume fraction. The well known excess optical absorption in fundamental absorption region can be also explained by the EMA. The Hall mobility is sublinearly proportional to the size of crystallites when the volume fraction of crystallite is kept the same, which is attributed to a fractal property of microcrystalline system.

1. Introduction
Mesoscopic and/or macroscopic inhomogeneities present in microcrystalline Si (μc-Si:H) prepared by chemical vapor deposition and hence the properties of electronic transport are quite complicated [1,2]. Although the influences of the grain size and the crystalline volume fraction on the electronic transport have been discussed, the detailed and quantitative natures are still not clear [1,3]. An existence of percolation path has been suggested for electronic transport in μc-Si:H films [1,3,4]. In fact, three-dimensional conductance network calculations (computer simulations) for the conductivity, $\sigma$, and the Hall mobility, $\mu_H$, show an existence of critical threshold of percolation path [5]. An effective medium approximation (EMA) can thus be suggested to be useful for explaining the transport properties quantitatively.

In the present study, the effective medium theory [6–8] which was developed long time ago is recalled to explain the dc conductivity, Hall mobility, and optical absorption in μc-Si:H. EMA calculates the conductivity of a random mixture of particles under the assumption that the inhomogeneous surroundings of a particle can be replaced by an effective medium. It is known that the EMA calculation coincides with the solutions for the bond percolation problem computed by a Monte Carlo sampling of a disordered network, except in the vicinity of the percolation threshold [6].

2. Effective medium approximation
The EMA predicts the total network conductance $\sigma_m$ in $D$ dimensions as

$$\left\langle \frac{\sigma - \sigma_m}{\sigma + (D - 1)\sigma_m} \right\rangle_\sigma = 0,$$

where $\sigma$ is a random value of conductivity. Under the assumption of a random mixture of particles of
two different conductivities, i.e. a volume fraction, \( C \), has a conductivity, \( \sigma_0 \), and the remainder a conductivity, \( \sigma_1 \), substantially less than \( \sigma_0 \), the simple forms of the dc conductivity and the Hall mobility, as a function of \( C \), have been obtained (see the pioneering works by Kirkpatrik [6] and Cohen and Jortner [7,8]). The EMA was extended to the a.c. conductivity in which \( \sigma \) in Eq. (1) is a complex admittance \( \sigma = \sigma_1 + i\sigma_2 \) [9]. As the optical constants are closely related to \( \sigma \), i.e. the complex dielectric constants, \( \varepsilon = \varepsilon_1 - i\varepsilon_2 = \sigma_2/\omega - i\sigma_1/\omega \), the optical absorption coefficient \( \alpha(\omega) \) can be also calculated through the relation of \( \alpha(\omega) = 4\pi\sigma(\omega)/cn \), where \( c \) is the light velocity and \( n \) the refractive index.

3. Application of the EMA to the experimental data

Solid circles in Fig.1 show the room temperature conductivity as a function of crystalline volume fraction, \( X_c \), for a series of undoped \( \mu \)-Si:H [1]. The solid line is calculated results for \( D = 3 \) followed by Cohen and Jortner [6], where \( \sigma_1 = 3 \times 10^{-9} (X_c = 0) \) and \( \sigma_0 = 3 \times 10^{-2} \) S cm\(^{-1} \) \((X_c = 1) \) were used (see Section 2). Although there is some scatter in the experimental data, the EMA calculation seems to replicate well the experimental data. Here the percolation threshold appears at \( X_c = 0.33 \) which agrees with the computer simulation \((X_c = 0.32) \) [5], while the critical threshold for phosphorus-doped \( \mu \)-Si:F:H is suggested to be \( X_c = 0.18 \) [10]. The scatter in experimental data might in part be due to the different grain sizes involved. In fact, it is known that the Hall mobility itself increases with increasing grain size [1], which will be discussed latter.

Solid circles in Fig. 2 show the room temperature Hall mobility in undoped \( \mu \)-Si:H as a function of volume fraction of crystalline Si [11]. The solid line is the calculated result based on Cohen and Jortner [6], where \( \mu_1 = 0.2 (X_c = 0) \) and \( \mu_0 = 2 \) cm\(^2\) V\(^{-1}\) s\(^{-1} \) \((X_c = 1) \) were used. Note, however, that \( \mu_1 = 0.2 \) used here could not reflect a true Hall mobility for pure amorphous state \((X_c = 0)\), since a double reversal in sign of the Hall effect has been observed in hydrogenated amorphous silicon (a-Si:H) [12]. The fitting of the calculation to the experimental data is reasonably good and the percolation threshold exists at \( X_c = 0.33 \). The small Hall mobility \((\sim 2 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) even approaching \( X_c = 1.0 \) is about two orders in magnitude smaller than that for doped single crystalline Si \((>100 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) [12]. This does not mean that the mobility of ‘crystalline’ itself is small. A microcrystalline material is composed of small crystallites joined together by grain boundaries (GBs) and carriers can be trapped into localized states in GBs, which reduces the mobility significantly [13].

It is known that the Hall mobility of \( \mu \)-Si:H increases linearly with increasing crystallite size \( \delta \) for almost the same \( X_c^1 \) [1,3] and can be explained by a GB trapping model in which thermionic
emission current is taken into consideration [12]. However, as shown in Fig. 3, a series of experimental data for the Hall mobility seems to be sublinearly proportional to crystallite size, $\delta'$, with $\gamma \approx 0.3$. Note that the experimental data [1,3] are replotted here as a function of $\delta^{0.3}$. An alternative explanation for the size effect of $\mu_H$ is given as follows.

Under the same $X_c$, the area of GBs (and hence the number of localized states in GBs) can be proportional to the surface to volume ratio $R_{SV}$. We hence predict that $\mu_H$ is proportional to $R_{SV}^{-1}$, since $\mu_H$ is expected to be inversely proportional to the area of GBs. As $R_{SV}$ is proportional to $\delta^\beta / \delta^\alpha$, where $\alpha = 2.0$ and $\beta = 3.0$ in Euclid space dimension and $\alpha < 2$ and $\beta < 3.0$ in fractal space, the relation of $\mu_H \propto \delta^\gamma$ with $\gamma = \beta - \alpha$ is predicted. Note that $\alpha$ and $\beta$ are called the fractal dimensions. In Euclid space dimension, $\mu_H$ should proportional to $\delta$, which can be given also by an alternative argument. The sublinear dependence, $\mu_H \propto \delta^{0.3}$, experimentally found can be attributed to a fractal nature of microcrystallines. Interestingly, the fractal dimensions of $\beta \approx 1.9$ and $\alpha \approx 1.6$ are predicted from a computer simulation for metallic clusters growing in thin films [14]. As the mobility can be dominated by GBs, larger Hall mobility can be obtained if the number of GB states could be reduced or passivated by some means.

Finally, the excess optical absorption in fundamental absorption region is discussed. A larger optical absorption coefficient for $\mu$-c-Si:H than for crystalline silicon (c-Si) from the infrared to the blue has been reported [3,15,16]. An example for this difference is shown in Fig. 4. Three solid lines are the experimental data for a-Si:H, $\mu$-c-Si:H, and c-Si. The calculations by EMA for $X_c = 0.8$, for $D = 3$, are shown by open circles. Note that $X_c \approx 0.8$ is expected for their samples [3]. The frequency (energy)-independent refractive index, $n_0 = 3.9$ for c-Si and $n_1 = 3.2$ for a-Si:H which can be given as the root of real part of optical dielectric constant, are assumed for calculation. The calculations replicate the experimental data except around 1.7 eV. I suggest that a mean field constructed by mixture of amorphous and crystalline states dominates the optical absorption in $\mu$-Si:H. The multiple scattering seems to be not dominant in this energy range, while the scattering of light in general cannot be completely ignored in the present system [16].

4. Conclusions

The effective medium approach replicates the conductivity and the Hall mobility of $\mu$-Si:H as a function of crystalline volume fraction. The electronic transport in $\mu$-Si:H films are shown to be

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1 Imagine, for example in Euclid space, a cubic with a length $\delta = L$. The total surface area for this cubic is $6L^2$. When it is divided into eight parts, i.e. $\delta = L/2$, the total surface area is $12L^2$. The total surface area (grain boundary) is thus expected to be inversely proportional to $\delta$, when the volume is kept the same $L^3$. 
dominated by percolation processes and critical threshold exists at $X_c = 0.33$. The Hall mobility is sublinearly proportional to the size of crystallite when the volume fraction of crystallite is kept the same, which is attributed to a fractal nature of the present microcrystalline system. The optical properties can also be interpreted well in terms of the effective medium percolation approximation.

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References