On the transport properties of microcrystalline silicon at low temperatures

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The dark and photoconductivity along with pulsed electron spin resonance have been measured over a wide temperature range with a high crystallinity hydrogenated microcrystalline silicon (μc-Si:H) sample. The transport mechanism in μc-Si:H is discussed based on these measurements. Striking similarities in the temperature dependences of the dark and photoconductivity between μc-Si:H and some well studied materials, such as hydrogenated amorphous silicon, suggest that at low temperatures hopping of carriers between localized states dominates the transport properties of μc-Si:H.

1. Introduction

As a potentially important material for realizing high-stability and high-efficiency low cost electronic devices such as solar cells and thin-film transistors [1,2], hydrogenated microcrystalline silicon (μc-Si:H) is attracting increasing attention. For an electronic material, carrier transport is undoubtedly among the most important properties. μc-Si:H is a mixed-phase system. It consists of crystalline grains and amorphous tissue regions. Thus, the transport in μc-Si:H is of great interest also from the pure physical point of view.

In discussing transport mechanisms in μc-Si:H one should clearly distinguish between highly doped samples and undoped or lightly doped samples. Heavily doped samples demonstrate metallic-like dc conductivity. It has been recently shown [3] that for such samples the spread of the observed mean carrier densities, dc conductivities, and Hall mobilities can be well accounted for by the model of two-phase inhomogenity assuming highly conducting crystalline grains and poorly conducting amorphous regions.

However, little is known about the carrier transport mechanism in undoped μc-Si:H. At temperatures close to room temperature, the dark conductivity and the thermoelectric power of undoped or lightly doped μc-Si:H resemble to a large extent the transport data for hydrogenated amorphous silicon (a-Si:H). It appears possible to adequately describe these high-temperature transport properties of μc-Si:H in terms of a homogeneous model similar to that developed for a-Si:H [3]. In particular, an adequate description of the Meyer–Neldel rule in μc-Si:H has been performed in the homogeneous model by just taking into account the statistical shift of the Fermi energy [3].

Much less is known about the transport properties of undoped or lightly doped μc-Si:H at temperatures considerably below room temperature. It was generally found that the dark conductivity of μc-Si:H does not exhibit a simple thermally–activated temperature dependence at low temperatures [4], and the reason is unclear. Below we present experimental data from the measurements of the dark and photoconductivity in μc-Si:H extended to low temperatures and the data of the pulsed electron-spin-resonance (ESR) [5]. Based on these data, possible transport mechanisms in μc-Si:H at low temperatures are discussed.

It seems difficult, if possible, at the present stage of research to search for the transport mechanism by purely theoretical considerations. The reason is the lack of information on the very basic properties of the material among which is the band structure of μc-Si:H. Some studies claim the band discontimuities between crystalline grains and amorphous tissue regions to be most pronounced in the valence band [6,7], whereas others ascribe the discontinuity mainly to the conduction band [8]. It is also not clear whether the concepts of mobility edge and of band tail with localized stated, developed for homogeneous disordered semiconductors, can be applied to μc-Si:H without substantial modifications.

Therefore we choose for our discussion the following approach. We compare the observed temperature dependences of the dark and photoconductivity of μc-Si:H with those predicted by the transport mechanisms in various disordered semiconductors, and discuss whether the transport mechanisms which predict the observed temperature dependences can take place in μc-Si:H. It appears that the transport properties of undoped or lightly doped μc-Si:H at low temperatures can be well accounted for in an approach which treats the system as completely homogeneous, similar to the description suggested recently for transport in undoped μc-Si:H at high temperatures [3].

2. Experimental details

The thin film μc-Si:H sample studied in this work was prepared from highly H_2-diluted SiH_4 using the conventional plasma-enhanced CVD method [9]. The substrate

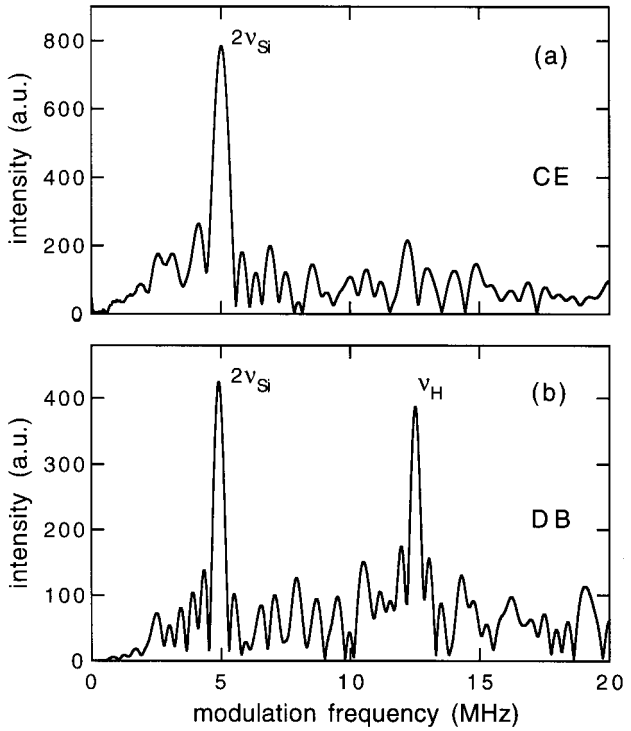

Figure 1. Fourier transform ESEEM spectra for CE (a) and DB (b) in μc-Si:H.

temperature was 250°C. The main characteristics of the sample are as follows: thickness $d = 0.42\,\mu$m, volume fraction of the crystallites $\rho = 90\%$, room temperature dark conductivity $\sigma_d(RT) = 1.5 \times 10^{-5}\,\Omega^{-1}\text{cm}^{-1}$, dark dangling bond density $N_{DB} = 1.4 \times 10^{16}\,\text{cm}^{-3}$. The crystallinity was measured by Raman scattering spectroscopy and confirmed by transmission electron microscope (TEM) observation. The two-pulse electron-spin-echo envelope modulation (ESEEM) measurement [10,11] was carried out using an ESR spectrometer operated at 8 GHz. The classical Hahn echo pulse sequence was used, $P(90°)$-τ-$P(180°)$-τ-echo, where τ is scanned. The conductivity of the sample was measured using a coplanar electrode configuration and the electrodes were Al evaporated on top of the film. For the photoconductivity measurements, a red laser (Ti-Sapphire, $\lambda = 710\,$nm) was used to illuminate the sample. The photoconductivity is defined as the difference between the total conductivity measured under illumination and the dark conductivity.

The TEM measurement revealed that the film had a columnar structure, with the crystallities extending to almost the entire thickness of the film. No clear amorphous regions could be seen between the grains due to the high (90°) crystallinity. Two ESR signals were observed in the sample: one is the dangling bond (DB) center at g=2.005 and the other is the conduction electron (CE) signal at $g = 1.998$. The ESEEM is capable of detecting the nuclear species surrounding the spin center [10,11], making use of hyperfine interactions between the electron spin and its surrounding nuclear spins, and thus gives information on the spatial distribution of the electron spins.

Fig. 1 shows the frequency domain ESEEM spectra for CEs and DBs in μ-Si:H obtained from the two-pulse ESEEM measurements. We find that for the CEs, only the double frequency of ^{29}Si nucleus appears, whereas for DBs both the double frequncy of ^{29}Si nucleaus and the fundamental frequency of ^{1}H nucleus appear. The fact that the CE echo decay is modulated by only Si nucleus and the DB echo decay is modulated by both Si and H nuclei indicates clearly that the CEs are located in low-H-concentration regions and the DBs in high-H-concentration regions. Given the structure of μc-Si:H, the above results are direct evidence that the CEs are located in the crystalline grains and the DBs in the grain boundary regions. The ESR results have important implications for carrier transport in μc-Si:H. The fact that

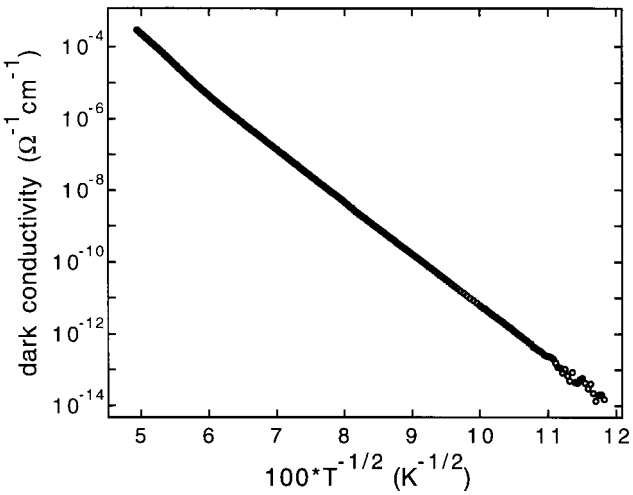

Figure 2. Temperature dependence of the dark conductivity.

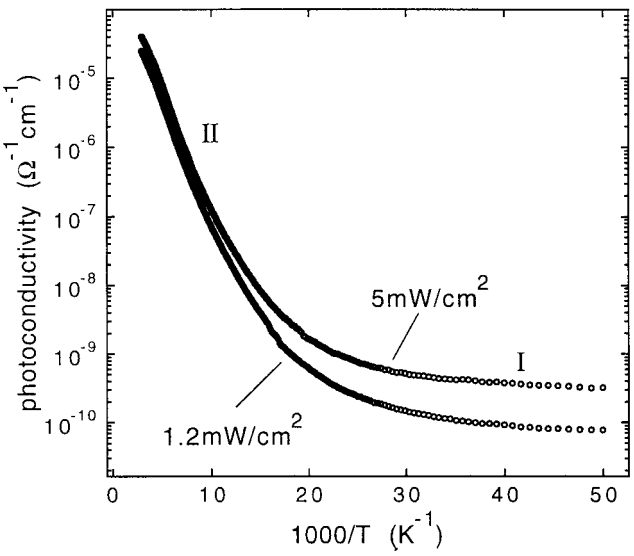

Figure 3. Temperature dependences of the photoconductivity at two light intensities.

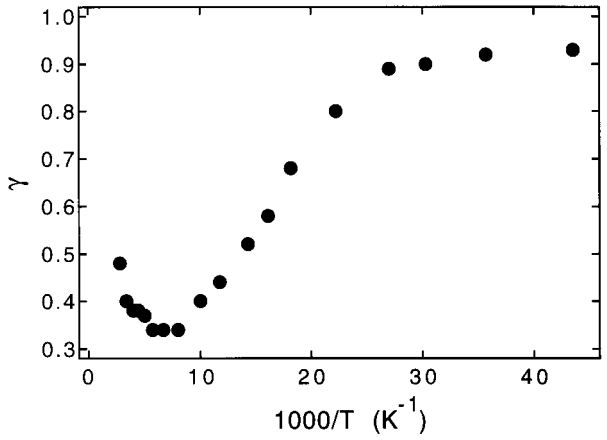

Figure 4. Temperature dependence of the exponent γ in the relation $\sigma_p \propto F^{\gamma}$.

the CEs prefer to reside in the grains implies that inside a grain the electrons are at a local energy minimum. In other words, electrons have to overcome an energy barrier when they move from one grain to another. Naturally, the energy barriers separating the grains are most likely to be the grain boundaries.

To get futher insights into the transport mechanism in μc-Si:H, we measured the dark (σ_d) and photoconductivity (σ_p) of the sample over a wide temperature range. Fig. 2 shows the T dependence of the dark conductivity σ_d. Below room temperature the data is well fitted with

$$\sigma_d \propto \exp[-(T_0/T)^{1/2}], \qquad (1)$$

where $T_0 \approx 2.6 \times 10^4$ K as determined between 80 and 120 K. The temperature dependences of σ_p is shown in Fig. 3 for two light intensities. Two regimes can be seen: the regime I below ~ 40 K where σ_p is essentially independent of T and the regime II above ~ 40 K where σ_p increases rapidly with T. From the intensity dependence $\sigma_p \propto F^{\gamma}$, where F is the light intensity, we found that the recombination is strongly T dependent. The temperature dependence of the parameter γ is shown in Fig. 4.

3. Discussion

As already mentioned, very little information is available regarding the band structure of μc-Si:H. Moreover, several rather contradictory reports have been published on the band edge discontinuities between crystalline silicon (c-Si) and a-Si:H [6–8]. From the measurements of the internal photoemission at c-Si/a-Si:H heterojunction, Mimura and Hatanaka [6] concluded that the major band edge discontinuity occurs in the valence band ($\Delta E_v = 0.71$ eV), while it is only 0.09 eV in the conduction band (ΔE_c). Cuniot and Marfaing [7], on the other hand, used a structure of c-Si / ⟨sputtered a-Si:H⟩ and found the discontinuity in the valence band negligible, with the main discontinuity existing in the conduction band. Xu et al. [8] found the discontinuity in the valence band $\Delta E_v \approx 0.26$ eV with a negligible discontinuity in the conduction band $\Delta E_c \approx -0.02$ eV between c-Si:H and a-Si:H. Under such circumstances it is not possible to discuss in detail the transport mechanism. Therefore we just discuss below the possible mechanisms which in principle could account for our experimental data, and specify the physical conditions for their realization.

We start with the dark conductivity, described by Eq. (1). Such a temperature dependence is well known for two classes of materials — granular metals and those in which transport is by variable-range hopping (VRH) with the density of states (DOS) in the vicinity of the Fermi level possessing a Coulomb gap. Since no information is available on the DOS and on the localization of states in the vicinity of the Fermi level in μc-Si:H, we do not want to speculate on the Coulomb gap and on the VRH mechanism. Moreover, in those systems, such as doped crystalline semiconductors, where VRH leads to the T dependence of the conductivity described by Eq. (1), thus T dependence is observed in a very narrow range of low temperatures due to the small width of the Coulomb gap (usually less than 1 meV [12]). Therefore it is unlikely that VRH is responsible for the observed T dependence of the dark conductivity.

The similarity to the dc current in granular metals is striking. In granular metals, the T dependence described by Eq. (1) is widely observed over a broad temperature range with $T_0 \approx 2 \times 10^4$ K [13,14]. There are some obvious structural similarities between μc-Si:H and granular metals. In both systems, grains are separated by a less conducting material and, as mentioned in the previous section regarding our ESR results, electrons have to overcome or to tunnel through an energy barrier when moving from one grain to another. Various mechanisms have been suggested to account for the T dependence by Eq. (1) for granular metals, among which the percolation model of Simanek [15] seems to be most plausible. However, all these mechanisms take into account just the temperature dependence of the carrier mobility $\mu(T)$, assuming the concentration of charge carriers $n(T)$ to be independent of temperature. Such a description can be applies to μc-Si:H provided that the Fermi energy is located above the mobility edge of the crystalline grains. In such a case the activated dc conductivity at high temperatures would correspond to thermal activation over the energy barriers separating the crystalline grains, whereas the T dependence described by Eq. (1) at lower T would be due to transport mechanisms similar to those in granular metals.

If, however, the Fermi energy in μc-Si:H is located in the region of localized states in the mobility gap, as typical for undoped or lightly doped disordered semiconductors, the conductivity arises from thermal excitation of carriers across the mobility gap into extended states or by hopping processes via localized gap states. Generally, the temperature dependence of the dc conductivity is determined by both $n(T)$ and $\mu(T)$

$$\sigma_d = e\mu(T)n(T). \qquad (2)$$

If one assumes that conduction via extended states dominates the transport, as suggested by Overhof and Otte [3] for high temperatures, $n(T)$ is the only temperature-dependent factor and

$$\sigma_d(T) = \sigma_0 \exp\Big\{-[E_c(T) - E_f(T)]/kT\Big\}, \qquad (3)$$

where σ_0 is a conductivity characteristic of transport in extended states (≈ 200 S/cm for a-Si:H [16]), $E_c(T)-E_f(T)$ is the difference in energy between the conduction level and the Fermi level. For transport in extended states, the T dependence described by Eq. (1) can appear only if $E_c(T) - E_f(T) \sim (kT)^{1/2}$. It is possible that such a relation is valid, and one can even try to search for a particular distribution of the DOS of localized states, which can provide such a relation, using, e.g., the model for the statistical shift of E_f suggested by Overhof and Beyer [16].

Another possibility is that transport in μc-Si:H at low temperatures is dominated by hopping processes via localized band tail states. In that case, some particular energy level $E_t(T)$ in the band tail is responsible for the dc current [17]. This temperature dependent transport energy is determined by the interplay between the two temperature dependent factors in Eq. (2). For localized states close in energy to the band edge, the mobility is higher but the concentration of electrons is lower than for deeper energy states. This transport level and hence the whole temperature dependence $\sigma_d(T)$ crucially depend on the form of DOS for localized states in the band tail[18]. For some particular form of DOS, hopping of electrons in the vicinity of the transport energy can, of course, give rise to the observed T dependence in Eq. (1). To find this particular DOS one should perform a series of computer simulations to those carried out in Ref. 17 with different forms of the DOS.

We now turn to discuss the temperature dependence of the photoconductivity (PC) shown in Fig. 3. The most remarkable feature of the PC is its similarity to the PC in a-Si:H [19]. At $T \lesssim 40$ K the magnitude of the PC essentially does not depend on temperature (regime I in Fig. 3) and at temperatures around 100 K the PC increases exponentially with temperature (regime II in Fig. 3). The PC of a-Si:H in the regime I is ascribed to the energy-loss hopping of photoexcited electrons and holes via localized band tail states [20]. In this regime, the charge carriers move by tunnel transitions to succesivily deeper localized states in the band tail. The rates of such transitions are not influenced by temperature, and hence the magnitude of the PC is temperature independent [20]. In a-Si:H, this energy-loss hopping is usually observed at $T \lesssim 40$ K [19]. It thus seems reasonable to assume that the same mechanism takes place in μc-Si:H as well. One could argue that in our μc-Si:H sample of 90% crystallinity, the number of localized band tail states is probably not as large as in a-Si:H for the same energy-loss hoping mechanism to work. However, the striking feature of the energy-loss hopping mechanism is that the conductivity is independent of the total density of the localized tail states [20]. Therefore it is not surprising at all that even the magnitude of the low-temperature photoconductivity of μc-Si:H is so close to that of a-Si:H.

If one assumes the energy-loss hopping mechanism for the low-temperature PC of μc-Si:H and a-Si:H, one should assume that the dark Fermi energy in μc-Si:H is located in the region of localized states as is the case in a-Si:H. If so, the temperature dependence of the dark conductivity $\sigma_d(T)$ cannot be determined solely by the temperature dependence of the carrier mobility $\mu(T)$. Hence it seems unlikely that the transport mechanism responsible for the temperature dependence of the dc current in granular metals can take place in μ-Si:H as well. Therefore one should try to explain the T dependence in Eq. (1) by using either the extended-state model of Overhof and Otte [3] or the transport-energy description of Gruenewald et al. [17].

It is worth nothing that the same two models — that of the transport energy [21] and that of the extended-states transport [22] have been suggested to describe the PC in a-Si:H at temperatures around 100 K. We do not think that it is possible to discriminate between these two approaches at the present stage of research, because even the band structure of μc-Si:H is not yet clear. But we think that it is resonable to search for the transport mechanism in undoped or lightly doped μc-Si:H at low temperatures in the framework of homogeneous transport models similar to those suggested for a-Si:H.

4. Conclusions

Dark and photoconductivity along with pulsed electron spin resonance have been measured with a μc-Si:H sample of 90% crystallinity over a wide temperature range below room temperature. At least three mechanisms can provide the observed temperature dependence of the dark conductivity:

(i) hopping mechanism for transport in granular metals with temperture dependent mobility and temperature independent concentration of carriers [13];

(ii) transport via extended states with temperature dependent concentration of mobile carriers and temperature independent mobility [16];

(iii) hopping transport via localized band tail states, where the interplay between the temperature dependent mobility $\mu(T)$ and the temperature dependent concentration of carriers $n(T)$ determine the transport path corresponding to the maximum of the product $\mu(T)n(T)$ and hence determine the conductivity [17].

However, the low-temperature photoconductivity of μc-Si:H shows such a striking similarity to that of a-Si:H that it seems reasonable to assume the same transport mechanism for μc-Si:H and a-Si:H. This excludes possibility (i) above, because it is known that in a-Si:H the concentration of carriers is temperature dependent at all temperatures, no matter whether transport is via extended states or by hopping through localized band tail states [21,22]. Therefore

our study suggests that it is reasonable to search for the transport mechanism in undoped or lightly doped μc-Si:H at low temperatures in the framework of homogeneous transport models similar to those suggested for a-Si:H. At very low temperatures ($\lesssim 40$ K), the energy-loss hopping seems to determine the photoconductivity in μc-Si:H. It is not possible, however, to discriminate between possibilities (ii) and (iii) for the photoconductivity at higher temperatures and for the dark conductivity, because neither the band structure of μc-Si:H, nor the DOS of localized states, or the value of the free carrier mobility are known for μc-Si:H.

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