PHYSICAL REVIEW B VOLUME 26, NUMBER 4 15 AUGUST 1982

Anomalous magnetoresistance in rf-sputtered hydrogenated amorphous silicon

P. Kuivalainen, J. Heleskivi, M. Leppihalme, U. Gyllenberg-Gästrin, and H. Isotalo
Semiconductor Laboratory, Technical Research Center of Finland, SF-02150 Espoo 15, Finland and Electron Physics Laboratory, Department of Electrical Engineering, Helsinki University of Technology, Otakaari 5 A, SF-02150 Espoo 15, Finland
(Received 2 February 1982; revised manuscript received 26 April 1982)

Magnetoresistance (MR) measurements for magnetic fields up to 10 T have been made on amorphous-silicon—hydrogen (a-Si:H) thin films prepared by reactive rf sputtering. The effect of a systematic decrease of the gap state and spin densities due to the hydrogenation on MR has been investigated. Electron-spin-resonance (ESR) and dark dc conductivity measurements, which give supporting information on the electrical behavior of a-Si:H, have also been made in the temperature range 30—500 K. The Movaghar-Schweitzer-Osaka hopping model, in which MR is a result of the magnetic field dependence of the spin-flip relaxation time of the charge-carrier spin, accounts well for the results at temperatures $T > 150$ K. With the fitting of this model to the MR results, values of the positive Hubbard-type repulsion energy U_{eff} for doubly occupied gap states near the Fermi level are obtained, $U_{\text{eff}}=0.21$ eV for the a-Si films and $U_{\text{eff}}=0.31-0.32$ eV for the a-Si:H films. It is concluded that the change of sign in MR at low fields with decreasing spin density is due merely to a narrowing in the distribution of the hopping relaxation times. Some of the parameters needed in the analysis of the MR results are determined by the fitting of Mott's variable range-hopping model to the conductivity data of the films with $N_s > 10^{18}$ spins cm^{-3}. Quite reasonable values of Mott's parameters are obtained if high values for jump-rate prefactors $\nu_0 = 10^{19}$ to 10^{20} s^{-1} are accepted, which values are also needed to account for the magnitudes of the MR effect and the ESR linewidth.

I. INTRODUCTION

The recent upsurge in interest in amorphous silicon (a-Si) and hydrogenated a-Si (Ref. 1) arises primarily from two sources. The first involves the possible technological applications in thin-film devices and solar photovoltaic energy conversion. The second impetus centers on answering fundamental questions about, e.g., the nature of electronic states and electrical transport in disordered semiconductors. One of the key problems is concerned with the role and origin of localized states in the forbidden energy gap. These states can arise from defects in the disordered network, i.e., dangling bonds, vacancies, and voids.

An important question is whether the gap states possess a positive or negative effective correlation energy U_{eff}. The Hubbard-type Coulombic repulsion between electrons in a doubly occupied gap state may be lowered in the amorphous semiconductors due to a polaronic distortion in local bonding, as first proposed by Anderson.[2] This distortion, i.e., the drawing together of the two atoms in the bond can in the case of chalcogenide glasses even lead to an attractive final Hubbard $U_{\text{eff}} < 0$. In tetrahedrally bonded amorphous semiconductors there may be in general a mixture of localized states with positive and negative U_{eff}. For a dangling bond in the threefold coordinated Si atom and for a Si-H-Si three-center bond, both positive and negative values of U_{eff} have been suggested in theoretical estimations.[3–5]

There is experimental evidence for both positive- and negative-U gap states in a-Si:H. Knights, Biegelsen, and Solomon[6] have concluded from their electron-spin-resonance (ESR) results that the negative-U centers may exist in glow-discharge a-Si:H. On the other hand, Street and Biegelsen[7] have performed light-induced ESR measurements which indicate that the primary defects in a-Si:H are dangling bonds with a positive correlation energy. The same result for the dangling bonds and the vacancy-type defects has been obtained by Voget-Grote *et al.*[8] from the ESR, photoluminescence, photoconductivity, and dark hopping conductivity measurements on evaporated a-Si. Recently Dersch, Stuke, and Beichler[9] studied the temperature dependence of the ESR spectra in doped glow-discharge *a*-Si:H. Their results were explained in a model with a large correlation energy, $U_{eff} \gg kT$, for the valence-band-tail states and a small one, $U_{eff} < kT$, for the conduction-band-tail states. To our best knowledge no one has, however, determined the value of U_{eff} in *a*-Si, although for the positive correlation energy a range $0 < U_{eff} < 0.8$ eV has been estimated.[10]

Some new and fascinating correlation appears to exist between electron spin and electrical conduction and recombination in amorphous semiconductors as illustrated by the phenomena of spin-dependent luminescence[11,12] and dark[13–22] and photomagnetoresistance.[23,24] Magnetic fields as small as a few gauss can significantly change the properties of these materials, which is quite unusual in the physics of semiconductors.[25] The anomalous dark magnetoresistance (MR) in the amorphous semiconductors Ge, GeTe, InSb, and Si was first observed by Mell and Stuke.[13] These materials show a completely different MR behavior as compared with the one in crystalline semiconductors, where the resistivity ρ typically increases by application of an external magnetic field. In the slightly doped crystalline semiconductors the relative increase of the resistivity $\Delta\rho/\rho(0)$, i.e., the positive MR is proportional to the square of the mobility μ and the magnetic field B_0,

$$\Delta\rho/\rho(0)=T(r)(\mu B_0)^2 \tag{1}$$

with a well-known[26] scattering-mechanism-dependent proportionality constant $T(r)$. The heavily doped crystalline semiconductors,[27] magnetic semiconductors,[29] and metal-oxide-semiconductor field-effect transistor (MOSFET) inversion layers[29] may exhibit a negative MR but usually at low temperatures only. Although the mobility in amorphous semiconductors is very low,[30] $\mu \lesssim 5\ \mathrm{cm^2/V\,s}$ even in the extended states, the MR measured by Mell and Stuke was exceptionally large already at low magnetic fields and it was negative even at high temperatures. Mell[14] found later both positive and negative MR in *a*-Si and showed that the former depends strongly on sample preparation. The anomalous MR in *a*-Si and *a*-Ge has been confirmed by several investigators.[15–22]

The electrical properties of the tetrahedrally bonded amorphous semiconductors are very sensitive to the preparation methods and conditions.[1,31] While the influence of hydrogen on optical, electrical, and magnetic properties of sputtered *a*-Si has extensively been studied, MR in sputtered *a*-Si has not been measured so far. The previous dark MR measurements on *a*-Si have been performed on hydrogen-free evaporated films[13,14,21,22] or on films prepared by a high-temperature chemical vapor deposition (CVD) method.[18] Further, the magnetic field range has been limited to low fields, $B_0 \lesssim 1$ T. In this paper we report the results of the MR measurements on rf-sputtered hydrogenated *a*-Si thin films extending the measurements to high magnetic fields, $B_0 \lesssim 10$ T. The influence of the systematic decrease of the gap state and spin densities due to hydrogenation on MR is investigated. We also make use of other experimental techniques (ESR and conductivity) which give supporting or complementary information concerning the electrical behavior of *a*-Si:H. The purpose is to clarify the proposed[21,32] relationship between MR, ESR, and conductivity.

The total absence of theory has been a major problem in most of the previous publications and it has clearly hindered detailed considerations of the magnetic-field-dependent transport in the amorphous semiconductors. A couple of years ago Movaghar and Schweitzer[32] proposed successfully a hopping model for the anomalous MR, which offers a good basis for systematics in MR studies as well as for a detailed analysis of the data. Osaka's improved version[33] of this model is utilized in the present work leading to estimates for several parameters related to the gap states in *a*-Si:H. Using the expressions for Mott's parameters derived by Paul and Mitra[34] we have evaluated with the aid of ESR results the influence of hydrogenation on the gap-state density at the Fermi level, the inverse rate of falloff of the wave functions associated with these states, the average hopping length and energy, and the maximum hopping frequency. These parameters are needed in the analysis of the MR results. Some of the preliminary results of our MR measurements on sputtered *a*-Si:H at low magnetic fields $B_0 < 1$ T have been reported earlier.[35]

II. EXPERIMENTAL METHODS

A. Sample preparation and characterization

Hydrogenated *a*-Si with good electronic properties can be produced by glow-discharge decomposition of silane or sputtering of Si in an argon-hydrogen plasma.[1,31] Our *a*-Si:H films were prepared by reactive rf sputtering, since it has the advantage of allowing independent control of the hydrogen content and thus, the spin and gap-state densities in the films without interfering with other film preparation parameters. A mixture of 20 vol % hydrogen in argon was diluted with pure argon to provide a hydrogen concentration from 0 to 20 vol % in the sputtering gas. The optical, electrical, and magnetic properties of the films prepared under various conditions were investigated in tens of samples. In the present paper we report the results of the MR measurements performed on the samples prepared under the following conditions: The total gas pressure was always 10 mTorr, the sputtering power was 5 W/cm^2, and the substrate temperature 250 °C. A cast polycrystalline silicon target was used and the films were deposited onto Corning 7059 glass substrates. The substrate to target distance was kept at 3 cm. We were mainly interested in the MR effect as a function of the gap-state and spin densities which are directly related to the MR effect and which can be accurately controlled by the hydrogen partial pressure in the sputtering gas. We have also made attempts to measure MR in glow-discharge *a*-Si:H films but without success (see below).

Thicknesses, deposition rates, spin densities, and room-temperature conductivities of the samples prepared in different hydrogen partial pressures and used in our MR, ESR, and conductivity measurements, are listed in Table I. These samples cover the spin-density range where the MR effect was measurable. Thickness measurements were made with an interference microscope and a Sloan-Dektak surface profilometer. The deposition rate was found to decrease with increasing hydrogen pressure as the hydrogen ions carry part of the current but do not contribute to the sputtering process. X-ray diffraction studies proved that our films were amorphous.

The incorporation of hydrogen in the films was monitored by infrared spectroscopy using a Perkin Elmer spectrometer (type 377). Infrared spectra which were studied between 200 and 2500 cm^{-1} displayed all the typical features found[36] in rf-sputtered *a*-Si:H prepared under similar conditions. The absorption doublet at 200 and 2100 cm^{-1} which is assigned to the stretching vibrations of Si-H and Si-H_2 bonds, respectively, shows that these configurations are present approximately in equal amounts. The wagging vibration of H atoms at 640 cm^{-1} caused the strongest ir absorption. From 800 to 1000 cm^{-1} there was a broad absorption probably due to oxygen[36] incorporation in the film.

Infrared spectroscopy is one of the methods[31] to determine the absolute hydrogen content C_H in the *a*-Si:H films, but it involves some controversial assumptions[31,37]. Furthermore, C_H is not a reliable parameter since the hydrogen may be incorporated in different ways into the material, leading to different properties for the same total hydrogen content.[38] We will continue to use the hydrogen partial pressure P_H and spin density N_s as experimental variables which both can be accurately measured. Moreover, N_s is closely related to the MR effect. Transmission measurements in the wavelength range 0.4 — 1.1 μm were performed in order to determine the optical energy gap E_g of the films. The absorption coefficient α was calculated as outlined by Freeman and Paul,[36] and the value of E_g was obtained as the intercept of the $\sqrt{\alpha h\nu}$ vs $h\nu$ plot with the $h\nu$ axis, where $h\nu$ is the photon energy. In hydrogen-free samples E_g was 1.5 eV and increased some tenths of an eV with increasing hydrogen pressure. The values of E_g in the most hydrogenated samples were confirmed by measuring the photoconductivity versus $h\nu$.

B. MR, ESR, and conductivity measurements

MR measurements in *a*-Si have previously been performed only in hydrogen-free[13,14,21,22] or doped[18] films which are rather well conducting. Since the hydrogenation decreases the conductivity by several orders of magnitude the MR measurements in *a*-Si:H become much more difficult due to the extremely high resistivity of the material, especially at low temperatures. Furthermore, the strong temperature dependence of the film resis-

TABLE I. Samples studied in the MR measurements.

Sample number	Partial hydrogen pressure P_H	Thickness (μm)	Deposition rate (Å/min)	Spin density (cm^{-3})	RT conductivity ($\Omega^{-1}\,cm^{-1}$)
1	0%	0.78	65	1.5×10^{20}	1.5×10^{-3}
2	2%	0.65	55	3.1×10^{19}	2.6×10^{-6}
3	5%	0.55	45	2.6×10^{19}	1.6×10^{-7}
4	10%	0.48	40	8.1×10^{18}	8.2×10^{-9}
5	20%	0.46	40	1.7×10^{18}	4.6×10^{-9}

tivity causes additional difficulties because even small temperature fluctuations may lead to resistivity changes much larger than the MR effect. A low-noise measuring system for low-conducting semiconductors has been constructed earlier[35,39] by which the MR effect was detectable also in the hydrogenated high-resistivity *a*-Si:H films even at low temperatures.

For the MR and conductivity measurements two aluminium electrodes were evaporated onto the films with a spacing of 1 mm. The width of the contacts was 2 mm. Owing to the high resistivity of the hydrogenated films the use of the four-point method was possible only in the hydrogen-free samples at high temperatures. All contacts showed Ohmic behavior in the electric field range $10-2\times10^3$ V/cm. In the MR measurements a constant voltage of 78.5 V supplied by dry batteries was applied across the coplanar gap of Al electrodes. The current through the samples was measured with a battery driven electrometer (Keithley 602), the output of which was connected to a voltage compensator and a recorder. All parts of the measuring system were enclosed by metal shields, whereby electrical currents down to a few 10^{-15} A could be detected. The MR measurements were possible at temperatures where the current was higher than 10^{-12} A. The samples were mounted into a cryostat in a vacuum better than 5×10^{-6} Torr. The magnetic field was produced by a low-noise 10-T superconducting magnet. The MR measurements were performed in two measuring sets by sweeping the magnetic field from 0 to 1 T and from 0 to 10 T, respectively. Every final data point corresponds to the mean of five or more measuring points taken from different magnetic-field-up runs.

The ESR measurements were performed with a Varian E-109 spectrometer at 9.1 GHz (*X* band). The microwave power was kept below 0.1 mW to avoid saturation and the modulation amplitude was smaller than 20% of the peak-to-peak linewidth. For the determination of spin densities in the *a*-Si:H films both a $10^{-3}M$ toluene solution and a EuSe standard with known numbers of magnetic moments were used giving consistent results.

III. RESULTS

Both the ESR linewidth ΔB and the spin density N_s of the *a*-Si:H films are significant parameters in the analysis of the MR data. The results from the ESR measurements on the samples listed in Table I are shown in Fig. 1. The well-known[1] strong decrease of N_s due to the incorporation of hydrogen in the films can be clearly seen. The peak-to-peak linewidth ΔB_{pp} vs N_s at room temperature shows the behavior observed earlier by Title, Brodsky, and Cuomo[40] in sputtered *a*-Si:H, i.e., ΔB_{pp} has a minimum in a certain spin-density range $N_s = 1-3\times10^{19}$ cm^{-3}. As discussed previously by, e.g., Movaghar and Schweitzer,[41] ΔB_{pp} in *a*-Si decreases with decreasing temperature especially in the films with highest N_s values, until ΔB_{pp} finally becomes T-independent at $T<200$ K. The T-independent $\Delta B_{pp}(0)$ measured in samples 1–4 slightly increases with decreasing N_s as shown in Fig. 1. The observed g value was 2.0055.

The temperature dependence of the dark dc conductivity σ_{dc} is shown in Fig. 2 for the films used in the MR measurements. At high temperatures $T>350$ K a single activation energy, 0.81 eV, describes the T dependence of σ_{dc} in the hydrogenated films. Figure 3 shows the low-temperature behavior of σ_{dc} and linear plots of $\log_{10}(\sigma_{dc}\sqrt{T})$ vs $1/T^{1/4}$. σ_{dc} decreases strongly with increasing P_H the total reduction being 5 orders or magnitude at $T<300$ K when N_s decreases from 10^{20} cm^{-3} to 10^{18} cm^{-3}. At very low temperatures σ_{dc} becomes

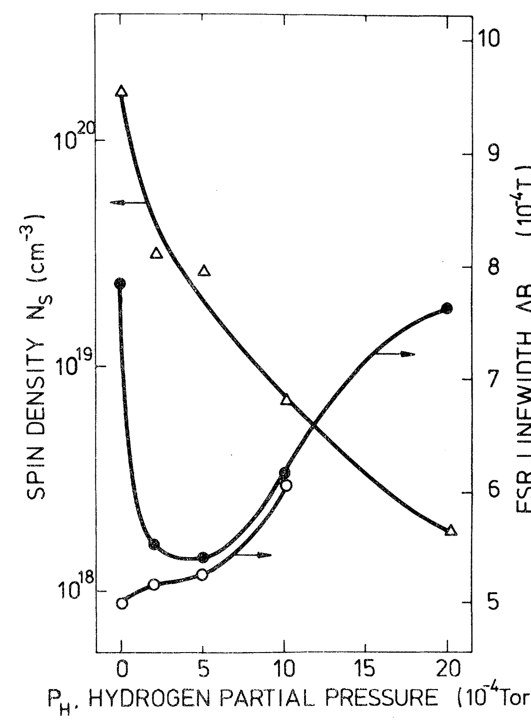

FIG. 1. Dependence of spin density (□), peak-to-peak ESR linewidth at room temperature (●), and temperature-independent linewidth at $T<170$ K (○) on hydrogen partial pressure in the sputtering gas.

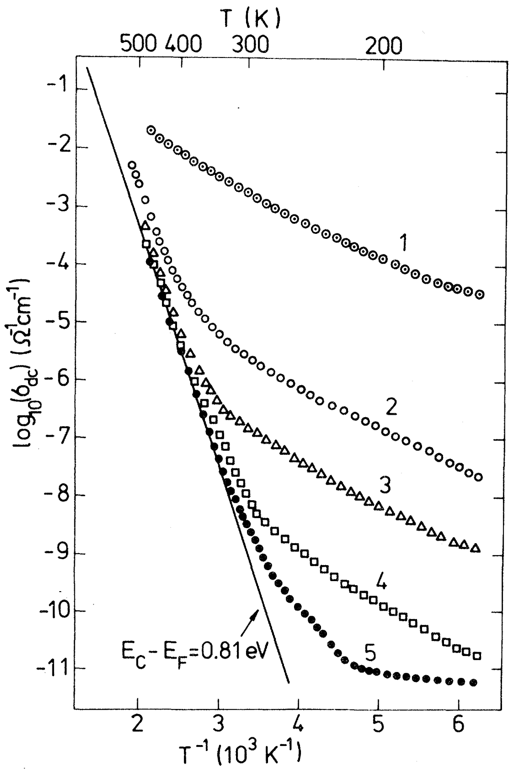

FIG. 2. Dark dc conductivity $\log_{10}\sigma$ vs reciprocal temperature $1000/T$. Numbers 1 to 5 refer to the samples listed in Table I.

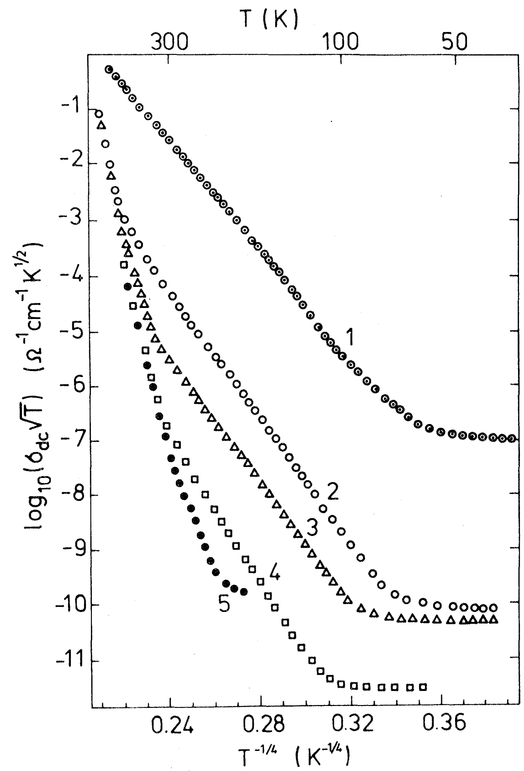

FIG. 3. Plot of $\log_{10}(\sigma T^{1/2})$ vs $T^{-1/4}$. Numbers 1 to 5 refer to samples listed in Table I.

almost T independent but its value still depends strongly on the hydrogenation.

The room-temperature MR versus external magnetic field is shown in Fig. 4 for low magnetic fields. In the film with the highest spin density, $N_s = 1.5\times10^{20}$ cm^{-3}, MR is negative. In the hydrogenated films with $N_s > 5\times10^{18}$ cm^{-3}, MR is positive, increasing steeply already at very low magnetic fields $\lesssim 0.1$ T and having a maximum at a field $B \approx 0.2$ T. The magnitude of this positive MR is more than an order of magnitude larger than the negative one. In sample 5 with the lowest spin density, MR was not measurable, i.e., $\Delta\rho/\rho(0)$ was smaller than 10^{-5}.

The results of the room-temperature MR measurements in the magnetic field range 0–10 T for samples 1–4 are shown in Fig. 5. MR changes from positive to negative in samples 2–4 at high enough fields. The crossover field shifts to higher values as the spin density of the film decreases.

MR versus magnetic field in sample 2 at various temperatures is shown in Fig. 6. The crossover point at which MR changes its sign shifts to higher magnetic fields with decreasing temperature. The same behavior can be seen in the results measured on the samples 3 and 4, Figs. 7 and 8, respectively. The positive contribution to MR increases with decreasing N_s. At low temperatures MR remained positive also at high magnetic fields and even increases with increasing field. The large value and the strong T dependence of the film resistivity at low temperatures prevented MR mea-

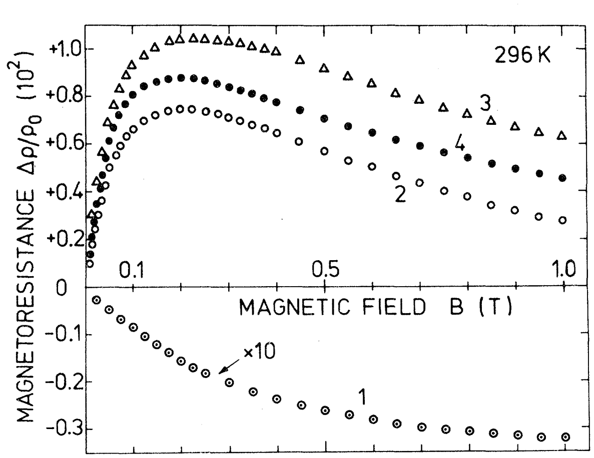

FIG. 4. Room-temperature magnetoresistance vs external magnetic field at low fields $B_0 \leq 1.0$ T. The numbers refer to samples 1, 2, 3, and 4.

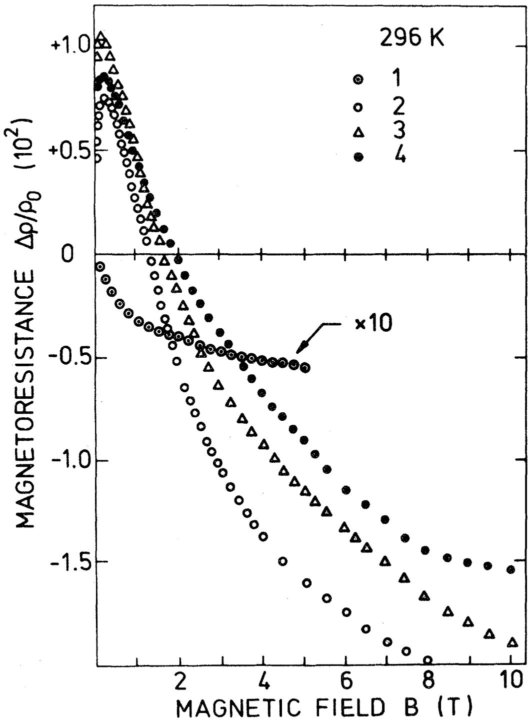

FIG. 5. Room-temperature magnetoresistance vs magnetic field for samples 1, 2, 3, and 4.

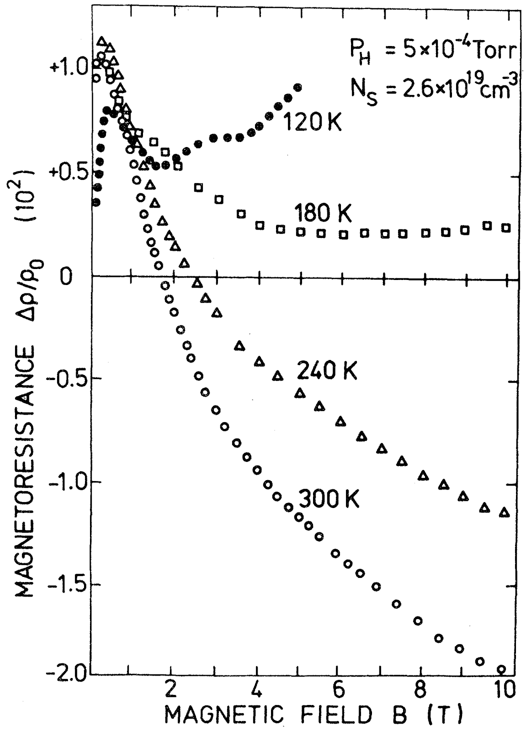

FIG. 7. Magnetoresistance vs magnetic field for sample 3 at various temperatures.

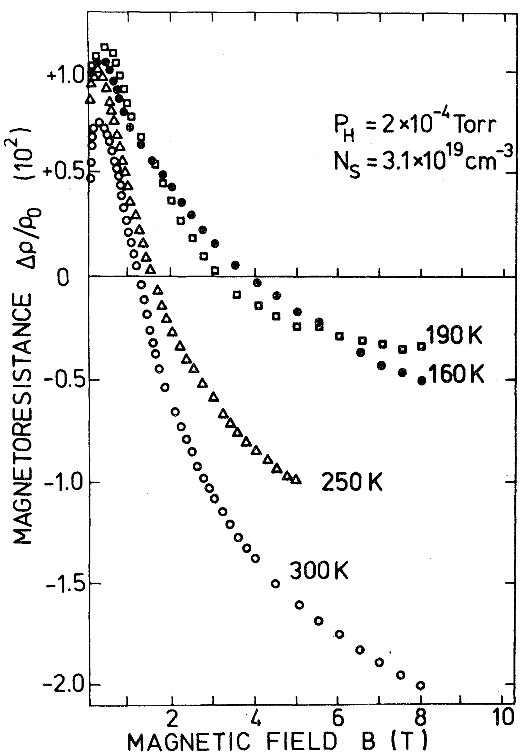

FIG. 6. Magnetoresistance vs magnetic field for sample 2 at various temperatures.

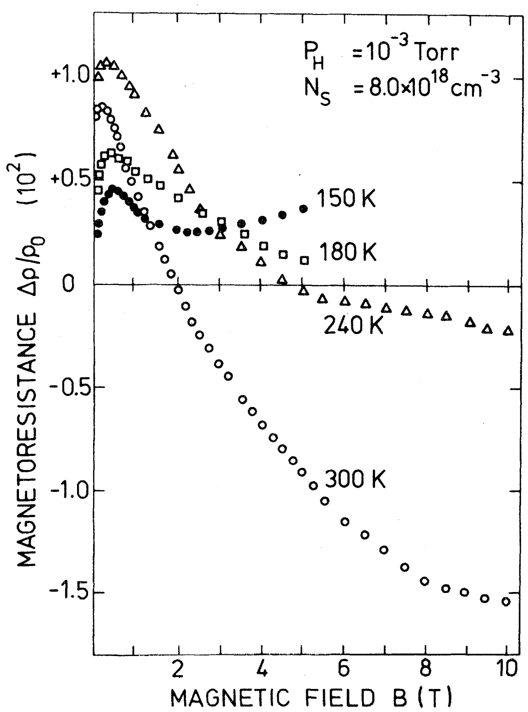

FIG. 8. Magnetoresistance vs magnetic field for sample 4 at various temperatures.

surements at higher fields, $B > 5$ T, since even small temperature fluctuations caused large changes in the resistivity during the long sweeping time of the superconducting magnet.

The temperature dependence of MR at low magnetic fields in samples 1–4 is shown in Fig. 9. The absolute value of the purely negative MR found in sample 1 increases with decreasing T in the whole temperature range studied in this work. The positive low-field MR versus T in samples 2, 3, and 4 has a maximum in the temperature range $200 < T < 300$ K. This maximum shifts to a higher temperature as the spin density of the films decreases.

IV. ANALYSIS OF CONDUCTIVITY AND ESR RESULTS

A. Dark dc conductivity

As recently pointed out by Anderson and Paul,[42] the nature of the charge transport in amorphous semiconductors is still poorly understood in spite of the vast investigations.[1] The dark dc conductivity $\sigma_{dc}(T)$ in sputtered a-Si follows below the room-temperature Mott's relation for variable range hopping,[43]

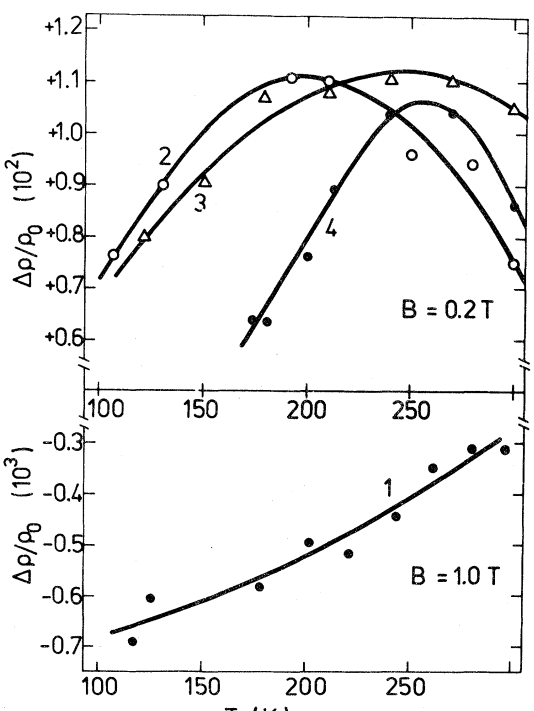

FIG. 9. Low-field magnetoresistance vs temperature for samples 1, 2, 3, and 4.

$$\sigma_{dc}(T)=\sigma_0 e^{-(T_0/T)^{1/4}} , \quad (2)$$

but there is no agreement about the physical interpretation of the parameters σ_0 and T_0. At high temperatures the current is believed to be carried by electrons thermally excited to the extended states of the conduction band. Indeed, $\sigma_{dc}(T)$ at high temperatures follows the general relation also proposed by Mott,[43]

$$\sigma_{dc}(T)=\sigma_1 e^{-(E_c-E_F)/kT} , \quad (3)$$

where E_c is the energy of the mobility edge and E_F is the Fermi energy. Figures 2 and 3 show that $\sigma_{dc}(T)$ measured on our sputtered a-Si:H films follows relation (2) at low temperatures, $T < 300$ K, and relation (3) at high temperatures. Previously $\sigma_{dc}(T)$ in sputtered a-Si:H has been studied by Anderson, Moustakas, and Paul[44] and Anderson and Paul[42] at high temperatures, $T > 200$ K. The results of the low-temperature σ_{dc} measurements in sputtered a-Si:H at $T \geq 100$ K have been reported by Zemek, Závetová, and Koc,[45] but no analysis of the results was made. We have extended the temperature scale further downwards, i.e., below 100 K as shown in Fig. 3. Since estimates for the parameters related to the electrical conduction are needed in the detailed discussion of the MR behavior, we have analyzed the low-temperature σ_{dc} results following the treatment of Paul and Mitra.[34]

First, however, we have to show that the measured σ_{dc} is really the bulk conductivity, i.e., the conduction is not due to surface effects such as band-bending in the film-substrate interface. As shown by Solomon, Dietl, and Kaplan[46] this band-bending effect is important in low-conducting hydrogenated a-Si because of the low carrier density. According to these authors the conductivity at high temperatures can be written

$$\sigma_{app}=\sigma_2\frac{\delta}{d}e^{-(E-qV_s)/kT}+\sigma_1 e^{-(E_c-E_F)/kT}$$
$$=\sigma_A+\sigma_B , \quad (4)$$

where σ_{app} is the apparent conductivity of the sample, σ_A the surface conductivity depending on the thickness d of the sample, the effective thickness δ, and the surface potential V_s. σ_B is the high-temperature bulk conductivity, Eq. (3). Solomon *et al.*[46] showed that a-Si:H has two states: state A with a conductivity dominated by $\sigma_A = 4\times 10^3$ $e^{-0.5\ \mathrm{eV}/kT}\ \Omega^{-1}\mathrm{cm}^{-1}$ and state B with a conductivity $\sigma_B = 10^5 e^{-0.87\ \mathrm{eV}/kT}\ \Omega^{-1}\mathrm{cm}^{-1}$, the state B being very close to the flat-band case, $\sigma_{app}=\sigma_B$.

In all a-Si:H films studied in the present work the high-temperature conductivity followed Eq. (3) with parameters $\sigma_1 \approx 10^5\ \Omega^{-1}\,\text{cm}^{-1}$ and $E_c - E_F = 0.81$ eV. Hence the above-mentioned model leads us to identify the state-*B* behavior even in our most hydrogenated films allowing us to neglect the surface effects in the analysis of our conductivity data.

An additional evidence for the bulk value of the pre-exponential factor σ_1 is obtained from Mott's[47] "minimum metallic conductivity" $\sigma_{\min} = 200 - 300\ \Omega^{-1}\,\text{cm}^{-1}$ which is related to σ_1 by $\sigma_{\min} = \sigma_1 e^{-\beta/k}$. Here β is the first-order expansion coefficient for the temperature dependence of $E_c - E_F = E(0) - \beta T$. Using the experimental value[48] $\beta = 5.2 \times 10^{-4}$ eV/K measured on sputtered a-Si:H one obtains for the preexponential factor σ_1 values which are close to our measured $\sigma_1 \approx 10^5\ \Omega^{-1}\,\text{cm}^{-1}$.

In order to see the influence of the hydrogenation on Mott's parameters they are evaluated from the curves of Fig. 3 at temperatures $100 < T < 300$ K using Eq. (2). The constants T_0 and σ_0 in Eq. (2) have the forms[34]

$$T_0 = \frac{\lambda \alpha^3}{k N(E_F)} \qquad (5)$$

and

$$\sigma_0 = e^2 R^2 \nu_0 N(E_F)\ , \qquad (6)$$

where

$$R = \left[\frac{9}{8\pi \alpha k T N(E_F)} \right]^{1/4} \qquad (7)$$

is the hopping distance, ν_0 a jump rate prefactor, k Boltzmann's constant, α the inverse rate of falloff of the wave function of a localized gap state, and $N(E_F)$ the density of the gap states at the Fermi level E_F. λ is a dimensionless constant and has a value ~ 18.1. Simultaneous solution of Eqs. (5)–(7) yields[34]

$$\alpha = (2.122 \times 10^{16}/\nu_0)(\sigma_0 \sqrt{T} \sqrt{T_0}) m^{-1} \qquad (8)$$

and

$$N(E_F) = (1.996 \times 10^{48}/\nu_0^3)[(\sigma_0 \sqrt{T}\,)^3 \sqrt{T_0}\,]\ , \qquad (9)$$

in units of $\text{cm}^{-3}\,\text{eV}^{-1}$ where $\sigma_0\sqrt{T}$ and T_0 are obtained from the experimental data. The average hopping energy is obtained[47] by the hopping distance R and the density of states $N(E_F)$,

$$W = \left[\frac{3}{4\pi R^3 N(E_F)} \right]. \qquad (10)$$

Using the experimental data of Fig. 3 we have evaluated the parameters (7)–(10) and the results are listed in Table II. The density of gap states $N(E_F)$ decreases strongly whereas the localization radius of the electrons $\sim \alpha^{-1}$, the hopping length R, and the average hopping energy W increase due to the hydrogenation. The values of $N(E_F)$ are comparable with the ones obtained by other methods.[49] The values of α^{-1} are of the order of the interatomic distance in Si which is what one expects for the deep gap states. Also the analysis[50] of paramagnetic data in a-Si favor atomic values, i.e., $\alpha^{-1} \approx 2$ Å. Furthermore Mott's requirements of the localized state model $\alpha R \gg 1$ and $W \gg kT$ are fulfilled.

The changes of Mott's parameters due to the hydrogenation of a-Si are similar to the changes due to annealing. The main reason for the unreasonable values for $N(E_F) \approx 10^{26} - 10^{28}\ \text{cm}^{-3}\,\text{eV}^{-1}$ and $\alpha^{-1} \lesssim 0.01$ Å obtained by Paul and Mitra[34] seems to be the use of a single-phonon frequency $\nu_0 \approx 10^{13}\ \text{s}^{-1}$ in Eqs. (8) and (9) estimated from the Debye temperature. As recently pointed out by Movaghar *et al.*[51] this common estimate for ν_0 is based essentially on intuitive arguments rather than quantitative calculations. The values of ν_0 listed in Table II were determined by fitting the density of states given by Eq. (9) to $N(E_F) = N_s / U_{\text{eff}}$ where the spin density N_s and the Hubbard repulsion energy U_{eff} were obtained from the ESR and MR measurements, respectively (see below). The high fre-

TABLE II. Mott's parameters for a-Si:H films. For details of the calculations of ν_0 see text.

Sample	H partial pressure P_H (%)	T_0 (10^8 K)	$N(E_F)$ ($\text{cm}^{-3}\ \text{eV}^{-1}$)	α^{-1} (Å)	R (Å)	W (eV)	ν_0 (s^{-1})
1	0	1.54	7.0×10^{20}	1.24	14.9	0.10	3.9×10^{20}
2	2	3.10	1.0×10^{20}	1.90	26.9	0.12	2.6×10^{20}
3	5	2.97	8.0×10^{19}	2.10	29.1	0.12	1.1×10^{19}
4	10	5.75	2.6×10^{19}	2.40	40.2	0.14	1.3×10^{20}
5	20		5.4×10^{18}				

quencies in Table II are in agreement with the ones[41] obtained from measurements of the ESR linewidth in evaporated *a*-Si and in our sputtered *a*-Si:H films when the results were analyzed (see below) by a model[41] based on variable-range hopping processes. Further, the analysis of our MR data indicates that when $T_0 \approx 10^8$ K ν_0 must be of the order of 10^{20} s^{-1} in order to account for the observed T and B dependences of MR. Reader[52] has deduced from ac conductivity measurements on evaporated *a*-Si an even higher value $\nu_0 \approx 10^{21}$ s^{-1} when the Austin-Mott model was used. All these results imply that ν_0 must be considerably enhanced from the usual one-phonon frequency, but there are difficulties in identifying the relevant physical processes responsible for this enhancement. Movaghar and Schweitzer[41] have proposed that multiphonon processes[53] neglected in Mott's model could increase ν_0, but it remains to be seen whether a more advanced transport theory which takes into account, e.g., polaron effects, could explain the increase in ν_0 by a factor of 10^6.

The temperature-independent conductivity at very low temperatures (Fig. 3) is similar to the results observed, e.g., in amorphous SiC by Nair and Mitra.[34] Owing to a small signal-to-noise ratio, the MR measurements were not possible in the temperature range where this T-independent σ_{dc} was observed. Hence we shall not consider this matter further in the present paper except to remark that the electric-field-dependent tunneling from localized to extended states proposed[34] for SiC can be excluded since the conductivity did not depend on the applied voltage.

B. ESR results

The MR effect depends very sensitively on a coupling between a hopping electron spin and the neighboring spins.[32] This coupling also determines the ESR linewidth $\Delta B_{pp}(T)$ in *a*-Si and *a*-Ge.[41] The total magnetic field acting on a spin in the gap state ψ_i is

$$B_i^\mu = (B_0^\mu)_i + (B_I^\mu)_i \ , \qquad (11)$$

$$(B_I^\mu)_i = B_{\mathrm{exch}}^\mu + B_{\mathrm{dip}}^\mu + B_{\mathrm{hyp}}^\mu + B_{\mathrm{so}}^\mu \ , \qquad (12)$$

where B_0^μ is the external magnetic field in a direction $\mu = x,y,z$ and B_I the local internal field which is a superposition of exchange, dipolar, hyperfine, and spin-orbit contributions. The effective spin lifetime $1/\bar{\tau}_s$ in the state ψ_i and further the ESR linewidth ΔB_{pp} are related to the hopping motion of the spins. The average lifetime broadening can be calculated[41] using the internal field B_I,

$$\frac{1}{\bar{\tau}_s} = \left[\frac{(\bar{B}_I^x)^2 + (\bar{B}_I^y)^2}{\omega_0^2 + 1/\bar{\tau}_h^2} + \bar{\gamma} \right] \frac{1}{\bar{\tau}_h} \sim \Delta B_{pp}(T) \ , \quad (13)$$

where $\omega_0 = g\mu_B B_0^z/\hbar$ and

$$1/\bar{\tau}_h = \nu_0 \exp[-T_0/T)^{1/4}]$$

is the average jump rate between two sites. $\bar{B}_I$ is the average internal field expressed in frequency units and $\bar{\gamma}$ is related to the average g shift δg due to the spin-orbit field B_{so}.

Following the treatment of Movaghar and Schweitzer[41] for the T-dependent linewidth one can show by Eq. (13) that in order to account for the measured high-temperature linewidth (Fig. 1) values $\nu_0 \approx 10^{20}$ s^{-1} are needed. These high values are in agreement with the ones obtained in the conductivity measurements (see Table II). The other parameters are $\bar{B}_I \approx 2 \times 10^{-4}$ T and $T_0 \approx 10^8$ K obtained from the analysis of our conductivity and MR results, and $\bar{\gamma} \approx 10^{-2}$ is estimated[41] from the average g shift.

The spin-density dependence of ΔB_{pp} (300 K) (Fig. 1) can also be accounted for by Eq. (13). The decrease of ΔB_{pp} in the range $N_s = 10^{20} - 3 \times 10^{19}$ cm^{-3} is due to the reduction of motion of hopping electrons between bonds, i.e., $1/\bar{\tau}_h$ in Eq. (13) decreases as T_0 increases (Table II). The observed increase of both the T-independent linewidth and ΔB_{pp} (300 K) with decreasing N_s is most probably due to the reduction of the motional narrowing effects.[40]

An important question in the analysis of the MR data is whether the internal field B_I on which the MR effect depends sensitively increases due to the hydrogenation. The N_s dependence of the T-independent linewidth $\Delta B_{pp}(0) \sim B_I^2$ in Fig. 1 shows that the possible increase of B_I is very small in the range $N_s = 2 \times 10^{19} - 10^{20}$ cm^{-3} where large changes in the MR effect were observed (Fig. 4). Furthermore, the decrease of ΔB_{pp} (300 K) (Fig. 1) with increasing T_0 indicates that the decrease in the factor $\exp[-(T_0/T)^{1/4}]$ in Eq. (13) dominates the possible small increase of B_I. This is a significant conclusion since the sign of the MR effect depends on the value of the product[32]

$$B_I^2 \exp[(T_0/T)^{1/4}] \ .$$

The spin density N_s obtained from the ESR measurements is closely related to the density of localized gap states[9,10,25] $N(E)$. For a given distribution $N(E)$ and Fermi-level position E_F the total number of spins is given by

$$N_s = \sum_i N(E_i) f(E_i) , \quad (14)$$

where $f(E_i)$ is the probability for single occupation of a localized state at E_i with correlation energy $U_{\text{eff}}(E_i)$,

$$f(E_i) = \frac{2e^{-(E_i - E_F)/kT}}{1 + 2e^{-(E_i - E_F)/kT} + e^{-[2E_i - 2E_F + U_{\text{eff}}(E_i)]/kT}} . \quad (15)$$

If the correlation energy is much larger than the thermal energy, $U_{\text{eff}} \gg kT$, and the density of states and $U_{\text{eff}}(E_i)$ are slowly varying functions of energy in the range $E_F - U_{\text{eff}} < E_i < E_F$, the spin density as estimated by Eqs. (14) and (15) reads

$$N_s \approx U_{\text{eff}}(E_F) N(E_F) . \quad (16)$$

This result was utilized in the analysis of conductivity data on our *a*-Si:H films as mentioned above. The Hubbard correlation energies $U_{\text{eff}} \approx 0.2 - 0.3$ eV $\gg kT$ were estimated from the results of the MR measurements.

V. INTERPRETATION OF MAGNETORESISTANCE RESULTS

The origin of the anomalous MR in amorphous semiconductors remained unexplained for several years after the first observation[13] of the effect. Attempts to explain it by invoking orbital shrinking spin-disorder scattering have been unsuccessful. The latter mechanism has been treated by Toyazawa[54] for heavily doped crystalline semiconductors on the basis of exchange scattering of the extended-state electrons due to localized spins in shallow donor states. The model was further developed by Khosla and Fischer[27] including higher-order terms in the scattering. Kawabata[55] has successfully explained the negative MR in doped crystalline semiconductors by a mechanism in which multiple scattering of electrons by impurities is suppressed by the applied magnetic field. None of these models can be applied to MR in amorphous semiconductors for the following reasons: (1) The extended state mobility[30] is too low, $\mu \lesssim 5$ cm^2/V s, (2) in the temperature range where the anomalous MR appears the conductivity is dominated by hopping processes in the localized states, and (3) these models are not able to describe the positive MR in *a*-Si and *a*-Ge. Even in the case of the negative MR an unrealistic value $\sim 10^3$ for the *g* factor is needed in the fitting[17,19] of the exchange-scattering model to the experimental data.

Hedgcock and Raudorf[56] have proposed a two-band model which assumes the existence of a band with high carrier mobility above a band with low mobility separated by a sharp mobility edge E_c between the two bands. On the application of a magnetic field the carriers are dumped into the high mobility band from the low mobility band resulting in a negative MR. In this model the ordinary decrease in the carrier mobility results in a positive contribution as described by Eq. (1). Mehra *et al.*[22] have qualitatively described the negative MR measured on their evaporated *a*-Si films by the two-band model. It seems to us, however, that much higher mobilities $\gtrsim 10^2$ cm^2/V s than the one measured[30] in *a*-Si, $\mu \lesssim 5$ cm^2/V s, are needed in order to obtain a quantitative agreement with the experimental data. Furthermore, the two-band model cannot explain the saturating positive component of MR in *a*-Si and *a*-Ge. One of the basic assumptions in this model is that the Fermi level E_F is close to the mobility edge E_c. In our *a*-Si:H films $E_c - E_F = 0.81$ eV as estimated from the high-temperature conductivity data (Fig. 2) by Eq. (3). This fact alone excludes the two-band model in the analysis of our MR data.

Since the hopping processes seem to dominate the electrical conduction in the temperature range where the MR effect is largest several authors[13,14,17] have tried to find a mechanism by which the applied magnetic field would modify the hopping rate. The shift of the gap state energies by a Zeeman energy $\pm\mu_B B_0$ where μ_B is Bohr's magneton, produces a hopping magnetoresistance[17]

$$\frac{\Delta\rho}{\rho_0} = 1 - \left[\cosh\left[\frac{\mu_B B_0}{kT}\right]\right]^{-1} \approx \frac{1}{2}\left[\frac{\mu_B B_0}{kT}\right]^2 . \quad (17)$$

It is clear from the experimental results that this mechanism cannot dominate the MR at low magnetic fields but at low temperatures and high fields it can contribute.

A couple of years ago Movaghar and Schweitzer[32] proposed a semiclassical random-walk hopping model which accounts partly for the previous experimental results. In this model the localized gap states near E_F are spread in energy with singly occupied gap states below E_F, doubly occupied states lying above E_F and empty states distributed randomly. An important consequence of the finite positive correlation energy U_{eff} for doubly occupied states is that excitations near the Fermi level can take place into empty as well as singly occupied states. The basic idea in the Movaghar-Schweitzer model is related to the fact that an electron which hops to an occupied state must have the correct spin orientation otherwise the transition is forbidden. In other words, when an electron makes a transition from one localized state to another which already carries a spin the final state must necessarily have singlet character (antiparallel spins). It is assumed that anomalous hops with simultaneous or nonsimultaneous spin-flip contribute to the hopping conduction. Then MR results from the magnetic field dependence of the spin-lattice relaxation time described by Eq. (13). Thus within the Movaghar-Schweitzer model the ESR linewidth and MR are very closely related to each other. This has been experimentally verified by Mell *et al.*[21]

The model was further developed by Osaka[33] who took explicitly into account the positive correlation energy $U_{\rm eff}$. He also included the percolation effects in the model and obtained for MR the result

$$\Delta\rho/\rho_0=\frac{[2+5e^{U_{\rm eff}/kT}/(T_0^h/T)^{1/4}]}{(T_0^h/T)^{1/4}}\left\{\frac{\bar{B}_I^2}{\nu_s^2}\left[1-\frac{\nu_s^2}{B_0^2}\ln\left[1+\frac{B_0^2}{\nu_s^2}\right]\right]-b^2\ln\left[1+\frac{B_0^2}{\nu_s^2}\right]\right\}, \tag{18}$$

where $\nu_s=\nu_0\exp-(T_0^h/T)^{1/4}$ is the hopping frequency for the singlet configuration, i.e., the hop rate without any spin flip. T_0^h is related to the width of the distribution of the hopping relaxation time and it is of the same order of magnitude[32] as the experimentally observed Mott's parameter T_0. $\bar{B}_I$ is the average internal magnetic field given by Eq. (12) and B_0 is the external magnetic field (both fields are expressed in frequency units). b is related to the average g shift,[32] $b^2=3\delta g^2/10$.

Expression (18) is valid only at high temperatures where

$$\nu_s=\nu_0e^{-(T_0^h/T)^{1/4}}\gg\bar{\tau}_s^{-1} \tag{19}$$

and

$$U_{\rm eff}/(T_0^h/T)^{1/4}\ll kT\ . \tag{20}$$

Condition (19) means that a hopping electron should see an essentially frozen-spin system, i.e., the hopping frequency must be much larger than the spin-flip frequency $\bar{\tau}_s^{-1}$ given by Eq. (13) at high temperatures. In the opposite case $\nu_s<\bar{\tau}_s^{-1}$ only the spin-polarization effect would remain which is of the order of $(\mu_B B_0/k_b T)^2$ as given by Eq. (17).

The MR expression (18) consists of a positive and a negative part and the sign of MR depends on the ratio $\bar{B}_I/\nu_0\exp[-(T_0^h/T)^{1/4}]$. So, the observed change of sign of MR from negative to positive (Fig. 4) due to the hydrogenation can result from either an increase of T_0^h caused by the decrease in the gap state density [$T_0\sim 1/N(E_F)$, Eq. (5)] or an increase in the internal field $\bar{B}_I$. If the hyperfine field $B_{\rm hyp}$ in Eq. (13) would dominate in $\bar{B}_I$ the incorporation of hydrogen in the a-Si film could increase B_I since a proton has a nonzero nuclear magnetic moment. Indeed, Mell *et al.*[21] found that doping of a-Si with In which has a large nuclear moment ($I=\frac{9}{2}$), increases $\bar{B}_I$ strongly and further changes the MR behavior. In our a-Si:H films a significant increase of $\bar{B}_I$ due to the hydrogenation seems to be improbable in the spin-density range where the change of sign in MR occurs, as concluded above in Sec IV B from the N_s dependence of the linewidth ΔB_{pp}. Additional evidence for this conclusion is obtained by fitting Eq. (18) to our MR results. The fitting procedure is the following: First a value for $U_{\rm eff}$ is chosen. Using the results of the conductivity and ESR measurements and Eqs. (5)–(10) and (16) the jump rate prefactor ν_0 (as well as other parameters in Table II) can be determined. Next B_I and T_0^h can be estimated in the case of the positive MR from the measured external magnetic field values $B_0^{(0)}$ and B_s, at which MR according to Eq. (18) becomes[33] zero, $B_I^2=2b^2\nu_s^2\ln(B_0^{(0)}/\nu_s)$, or saturates[33] at low fields, $B_s\approx 6h\nu_s\exp[(-T_0^h/T)^{1/4}]/g\mu_B$, respectively. In the case of the negative MR (sample 1) when there is no change of sign, only an upper bound for B_I can be estimated. Finally, a value for MR at given temperature and magnetic field can be calculated by Eq. (18). This procedure is repeated by using $U_{\rm eff}$ as a fitting parameter until the calculated values for MR agree with the measured ones. The fitting was possible only in a narrow temperature range around room temperature since at lower temperatures condition (19) becomes invalid (see below) and at high temperatures the band conduction described by Eq. (3) starts to dominate decreasing MR and making the fitting unreliable.

Figure 10 shows the calculated results for sam-

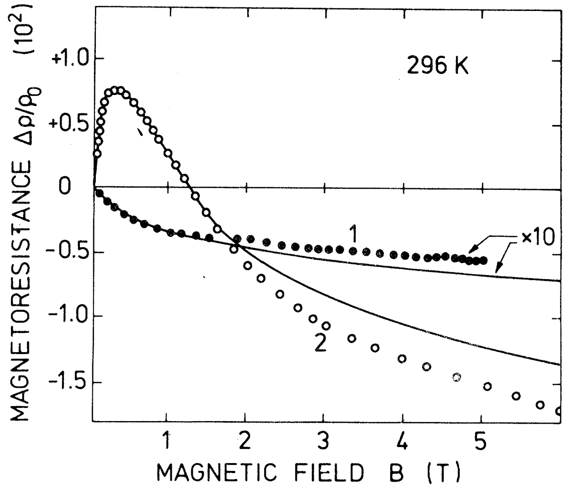

FIG. 10. Magnetoresistance vs magnetic field for samples 1 (●) and 2 (○). Solid curves have been calculated using Eq. (18).

ples 1 and 2 at room temperature. The agreement with the experimental results is excellent at low fields $B_0 < 2$ T. Strictly speaking the model is valid only at low fields since all the high-field effects such as spin polarization and a shift of the Fermi level have been neglected.[32,33] The values of the parameters T_0^h and $U_{\rm eff}$ for different samples are listed in Table III. The values for T_0^h are of the same order of magnitude as Mott's parameters T_0 in Table II obtained from the conductivity data. Also the increase in T_0^h with decreasing spin density is a common trend both in T_0^h and T_0. As pointed out by Movaghar and Schweitzer[32] the quantity T_0^h which describes the inverse of the width of the hopping relaxation time distribution, is related to Mott's T_0 but need not be exactly the slope obtained in the conductivity measurements. An obvious reason for this difference is the fact that the doubly occupied sites, for which α can be substantially smaller than for singly occupied sites, contribute more to the MR effect than to the dc conductivity.

The positive correlation energies $U_{\rm eff}$ in Table

TABLE III. Values for T_0^h and the correlation energies $U_{\rm eff}$ obtained from the measurements.

Sample	T_0^h ($\times 10^8$ K)	$U_{\rm eff}(E_F)$ (eV)
1	1.09	0.21
2	1.24	0.31
3	1.32	0.32
4	1.37	0.31

III are in an order of magnitude agreement with the range 0.1 eV $< U_{\rm eff} < 0.7$ eV estimated[10] for deep gap states. It is interesting to note that the experimentally[57] determined positive correlation energies for the localized states in small multivacancy complexes in irradiated crystalline Si lie in the range 0.25–0.39 eV. Adler[4] has also estimated a Coulombic correlation energy $U = 0.3$ eV for a dangling bond in a-Si by the difference in energies of double donors in crystalline Si. Thus we may conclude that the order of magnitude of $U_{\rm eff}$ in Table III can be accounted for by a Coulombic repulsion and the attractive contribution due to the possible lattice distortion seems to be of minor importance.

The reason for the increase in $U_{\rm eff}(E)$ from 0.2 to 0.3 eV due to the incorporation of hydrogen into the film remains uncertain to some extent. It has been proposed[10] that the correlation energy $U_{\rm eff}(E)$ below and around midgap depends on the gap-state energy E as $U_{\rm eff}(E) \sim |E - E_v|^\gamma$, where E_v is the mobility edge in the valence band and $\gamma < 1.0$. Since the hydrogenation enlarges the optical gap $E_g = E_c - E_v$ in a-Si:H but the conductivity activation energy $E_c - E_F$ remains unchanged (Fig. 2), one can conclude that $E_F - E_v$ and further $U_{\rm eff}(E_F)$ should increase with increasing hydrogen content in the film. However, this would imply a decrease in the localization length $\sim \alpha^{-1}$ due to the hydrogenation whereas the values in Table II obtained from the analysis of the conductivity data increase. Allan and Joannapoulos[5] have estimated that the formation of Si-H-Si three-center bonds in the hydrogenation would increase $U_{\rm eff}$.

For the internal field B_I a value 2×10^{-4} T was obtained in the hydrogenated films and an upper bound 4×10^{-4} T in the hydrogen-free film. These values are of the same order or magnitude as the ones needed to account for the temperature-independent linewidth $\Delta B_{pp}(0)$ (Sec. IV B). Also Bachus *et al.*[58] have obtained a value $B_I = 2\times 10^{-4}$ T in the analysis of their results of the ESR measurements on glow-discharge a-Si films. It is interesting to note that a classical dipolar interaction in the homogeneous spin system with a density $N_s \approx 3\times 10^{19}$ cm^{-3} leads[41] to $B_I \approx 2\times 10^{-4}$ T.

The experimental results in Fig. 9 show that the positive MR at low fields decreases with decreasing T at $T \lesssim 250$ K whereas the model or Eq. (18) predicts the opposite behavior. This disagreement is due to the fact that condition (19) is not valid at low temperatures which leads to a reduction of the contribution of the present mechanism. We can estimate from the measured T-independent linewidth $\Delta B_{pp}(0)$ (Fig. 1) and the obtained values for T_0^h (Table III) the temperature T^c at which condition (19) certainly becomes invalid, i.e., $\nu_s(T^c) \leq 1/\overline{\tau}_s \sim \Delta B_{pp}(0)$. In this way we obtain the lower limits for $T^c = 206$, 232, 244, and 259 K in samples 1, 2, 3, and 4, respectively. In the hydrogenated films these values of T^c lie in the temperature range where the maxima in MR occur in Fig. 9. Furthermore, the shift of the maximum to higher temperatures with decreasing spin density can be fully accounted for by the increase in T_0^h. This increase also explains the change of sign of MR (Fig. 4) and the shift of the field $B^{(0)}$ at which MR becomes zero (Fig. 5) to higher values. At a given spin density or value T_0^h the shift of the field $B^{(0)}$ to higher values with decreasing temperature (Figs. 6–8) results from the increase in the factor $\exp(T_0^h/T)^{1/4}$ in Eq. (18).

We may state that expression (18) and the dependence of its parameters on the hydrogenation account well for most of the details in the anomalous MR measured in our a-Si:H films. However, at low temperatures and at high magnetic fields, $B_0 > 2$ T, there is a strong positive MR effect, $\Delta\rho/\rho_0 \sim B_0^n$ with $n \geq 1$. This behavior, which is most clearly seen in Fig. 7 at $T = 120$ K, is incompatible with the one described by Eq. (18). There are several mechanisms which may contribute to this positive high-field MR: (1) the Zeeman splitting of the gap-state energies, i.e., MR given by Eq. (17), (2) shrinking of the hopping-electron orbit due to B_0, and (3) a shift of the Fermi level E_F due to B_0. Mechanism (1) does not seem to dominate since the small MR value $\sim 5\times 10^{-4}$ calculated by Eq. (17) at $T = 120$ K, $B_0 = 5$ T, is about an order of magnitude smaller than the observed effect. Mechanism (2) has been treated by Mikoshiba[59] in the case of shallow donor impurities in crystalline Ge. As pointed out by Mell[14] the distribution of hopping lengths R in amorphous semiconductors could according to Mikoshiba's theory lead to the positive MR, $\Delta\rho/\rho_0 \sim B_0^n$ with $n \lesssim 2$. This is in qualitative agreement with the observed MR behavior in Fig. 7 at $T = 120$ K, $B_0 > 2$ T. However, the order of magnitude of mechanism (2) in the case of hopping conduction through well localized gap states remains open. Also mechanism (3) which according to Mott and Davies[60] results in a change

$$\Delta\sigma = 0.5 \left[\frac{\partial^2 \sigma}{\partial E^2} \right]_{E=E_F} (\mu_B B_0)^2$$

in the conductivity, usually gives a positive contribution to MR, but a detailed knowledge of the energy dependence of the density of states near the Fermi level E_F is needed for the estimation of its magnitude.

The lack of MR in sample 5 with the lowest spin density can be accounted for by the domination of the band conduction in the whole temperature range studied, i.e., $\sigma_{dc}(T)$ did not follow Eq. (2) and no hopping MR could be detected. Since the extended state mobility μ in a-Si is very low[30] the ordinary positive MR described by Eq. (1) was too small to be measured. The same explanation applies to our glow-discharge samples which show a T-dependent conductivity similar to the one in sample 5 and no MR effect could be detected.

VI. SUMMARY

We have shown that MR measurements can give valuable information about gap states in a-Si:H which is not available from ESR and conductivity measurements alone. The Movaghar-Schweitzer-Osaka (MSO) hopping model which closely relates the anomalous MR to the ESR linewidth, accounts well for our high-temperature $T > 150$ K MR data. The model explains in detail the magnetic field, temperature, and spin-density dependences of the measured MR. Furthermore, it gives the correct order of magnitude for the MR effect with reasonable values of parameters which are supported by the results obtained by other experimental techniques. Since our MR results at low magnetic field in hydrogenated a-Si are similar to the results obtained by others[21] in hydrogen-free films with corresponding spin densities, we believe that the spin density or the density of gap states, not the hydrogen content in the film, is the most important parameter which determines, e.g., the sign of the MR effect. Both the ESR and MR results indicate that the internal magnetic field experienced by a spin in a gap state does not increase significantly due to the hydrogenation. Hence the observed narrowing of the width of the hopping relaxation time distribution, i.e., the increase of the Mott parameter T_0^h, completely accounts for the change of sign of MR due to the hydrogenation. Further, the strong dependence of MR on T_0^h in the MSO model and the observed increase of T_0^h with decreasing spin density N_s explain the sensitivity of the positive MR to the film-preparation conditions, which determine N_s.

To conclude we may state that the obtained MR data provide additional evidence for the idea that spin-dependent effects have a strong influence on the electrical transport in hydrogenated amorphous silicon.

ACKNOWLEDGMENTS

The authors wish to express their gratitude towards Professor T. Stubb, head of the Electron Physics Laboratory, for stimulating interest and support. Special thanks are due to Professor K. Yamada for assistance with the design of our measuring system for low-conducting materials, and to F. Sundholm for assistance with ESR experiments. One of us (P.K.) gratefully acknowledges the financial support by the Emil Aaltonen Foundation. This work was supported by the Finnish Academy of Sciences.

---

[1]For a review, see, e.g., *Amorphous Semiconductors,* Vol. 36 of *Topics in Applied Physics,* edited by M. H. Brodsky (Springer, Berlin, 1979); and Ref. 31.

[2]P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[3]R. Fisch and D. C. Licciardello, Phys. Rev. Lett. 41, 889 (1978).

[4]D. Adler, Phys. Rev. Lett. 41, 1755 (1978).

[5]D. C. Allan and I. D. Joannopoulos, Phys. Rev. Lett. 44, 43 (1980).

[6]J. C. Knights, D. K. Biegelsen, and I. Solomon, Solid State Commun. 22, 133 (1977).

[7]R. A. Street and D. K. Biegelsen, J. Non-Cryst. Solids 35-36, 651 (1980).

[8]U. Voget-Grote, W. Kümmerle, R. Fischer, and J. Stuke, Philos. Mag. B 41, 127 (1980).

[9]H. Dersch, J. Stuke, and J. Beichler, Phys. Status Solidi B 107, 307 (1981).

[10]H. Overhof and W. Beyer, Phys. Status Solidi B 107, 207 (1981); L. Schweitzer, M. Grünewald, and H. Dersch, Solid State Commun. 39, 355 (1981); J. D. Cohen, J. P. Harbison, and K. W. Wecht, Phys. Rev. Lett. 48, 109 (1982).

[11]D. K. Biegelsen, J. S. Knights, R. A. Street, C. Tsang, and R. H. White, Philos. Mag. B 37, 477 (1978).

[12]K. Morigaki, D. J. Dunsten, B. C. Cavenett, P. Dawson, and J. E. Nicholls, Solid State Commun. 26, 981 (1978).

[13]H. Mell and J. Stuke, J. Non-Cryst. Solids 4, 304 (1970).

[14]H. Mell, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, 1973,* edited by J. Stuke and W. Brenig (Taylor & Francis, London, 1974), p. 203.

[15]S. C. Agarwal and H. Fritzsche, Bull. Am. Phys. Soc. 15, 244 (1970).

[16]J. Kubelik and A. Triska, Czech. J. Phys. B 23, 123 (1973).

[17]A. H. Clark, M. H. Cohen, M. Campi, and H. P. D. Lanyon, J. Non-Cryst. Solids 16, 117 (1974).

[18]M. Taniguchi, M. Hirose, and Y. Osaka, J. Cryst. Growth 45, 126 (1978); M. Taniguchi, Y. Osaka, and M. Hirose, J. Electron. Mater. 8, 689 (1979).

[19]A. F. Khokhlov and O. N. Filatov, Fiz. Tekh. Poluprovodn. 13, 2223 (1979) [Sov. Phys.—Semicond. 13, 1300 (1979)].

[20]A. Yoshida, S. Nakashima, and M. Ieda, J. Non-Cryst. Solids 35-36, 421 (1980).

[21]H. Mell, L. Schweitzer, and U. Voget-Grote, J. Non-Cryst. Solids 35-36, 639 (1980).

[22]R. M. Mehra, S. C. Agarwal, S. Rani, R. Shyam, and P. C. Mathur, Thin Solid Films 76, 379 (1981).

[23]H. Mell, B. Movaghar, and L. Schwietzer, Phys. Status Solidi B 88, 531 (1978).

[24]H. Mell and B. Movaghar, J. Non-Cryst. Solids 35-36, 761 (1980).

[25]I. Solomon in Ref. 1, p. 189.

[26]K. Seeger, *Semiconductor Physics* (Springer, Wien, 1973), p. 75.

[27]R. P. Khosla and J. R. Fischer, Phys. Rev. B 2, 4084 (1970).

[28]R. Faymonville, P. Grosse, D. Mützenich, J. Heleskivi, and M. Mäenpää, J. Appl. Phys. 50, 1914 (1979).

[29]Y. Kawaguchi and S. Kawaji, J. Phys. Soc. Jpn. 48, 699 (1980).

[30]P. G. Le Comber, A. Madan, and W. E. Spear, J. Non-Cryst. Solids 11, 219 (1972); J. Dresner, Appl. Phys. Lett. 37, 742 (1980).

[31]J. C. Knights and G. Lucovsky, CRC Crit. Rev. Solid State Sci. 9, 211 (1980).

[32]B. Movaghar and L. Schweitzer, J. Phys. C 11, 125 (1978).

[33]Y. Osaka, J. Phys. Soc. Jpn. 47, 729 (1979).

[34]D. K. Paul and S. S. Mitra, Phys. Rev. Lett. 31, 1000 (1973); K. Nair and S. S. Mitra, J. Non-Cryst. Solids 24, 1 (1977).

[35]P. Kuivalainen, J. Heleskivi, M. Leppihalme, and U. Gyllenberg-Gästrin, in Proceedings of the Nordic Solid State Physics Conference, Copenhagen, 1981 [Phys. Scr. 25, 832 (1982)].

[36]E. C. Freeman and W. Paul, Phys. Rev. B 18, 4288 (1978).

[37]C. J. Fang, K. J. Gruntz, L. Ley, M. Cardona, F. J. Demond, G. Müler, and S. Kalbitzer, J. Non-Cryst. Solids 35-36, 255 (1980).

[38]E. C. Freeman and W. Paul, Phys. Rev. B 20, 716 (1979).

[39]The design and construction of our measuring system for MR and conductivity measurements in low-conducting materials was carried out in close cooperation with Professor K. Yamada from Saitama University, Japan.

[40]R. S. Title, M. H. Brodsky, and J. J. Cuomo, in *Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977,* edited by W. E. Spear (University of Edinburgh Press, Edinburgh, 1977), p. 424.
[41]B. Movaghar and L. Schweitzer, Phys. Status Solidi B 80, 491 (1977); B. Movaghar, H. Overhof, and L. Schweitzer, in *Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977,* edited by W. E. Spear (University of Edinburgh Press, Edinburgh, 1977), p. 419.
[42]D. A. Anderson and W. Paul, Philos. Mag. B 44, 187 (1981).
[43]N. F. Mott, Adv. Phys. 16, 49 (1967); Philos. Mag. 19, 835 (1969).
[44]D. A. Anderson, T. D. Moustakas, and W. Paul, in *Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977,* edited by W. E. Spear (University of Edinburgh Press, Edinburgh, 1977), p. 334.
[45]J. Zemek, M. Závetová, and S. Koc, J. Non-Cryst. Solids, 37, 15 (1980).
[46]I. Solomon, T. Dietl, and D. Kaplan, J. Phys. (Paris) 39, 1241 (1978).
[47]N. F. Mott, Philos. Mag. 26, 1015 (1972); 30, 513 (1974).
[48]J. Tardy and R. Meaudre, Solid State Commun. 39, 1031 (1981).
[49]P. G. LeComber and W. E. Spear in Ref. 1, p. 251.
[50]B. Movaghar, in Proceedings of the 22nd Scottish Summer School on Amorphous Magnetism, Dundee, 1981 (in press).
[51]B. Movaghar, B. Ries, and L. Schweitzer, Philos. Mag. B 41, 141 (1980).
[52]G. Rieder, Phys. Rev. B 20, 607 (1979).
[53]D. Emin, Phys. Rev. Lett. 32, 303 (1974).
[54]Y. Toyazawa, J. Phys. Soc. Jpn. 17, 986 (1962).
[55]A. Kawabata, J. Phys. Soc. Jpn. Suppl. A 49, 375 (1980).
[56]F. T. Hedgcock and T. W. Raudorf, Solid State Commun. 8, 1819 (1970).
[57]A. H. Kalma and J. C. Correlli, Phys. Rev. 173, 734 (1968); G. D. Watkins and J. W. Corbett, Phys. Rev. 138A, 543 (1965).
[58]R. Bachus, B. Movaghar, L. Schweitzer, and U. Voget-Grote, Philos. Mag. B 39, 27 (1979).
[59]N. Mikoshiba, Phys. Rev. 127, 1962 (1962).
[60]N. F. Mott and E. A. Davies, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1971), p. 181.