PHYSICAL REVIEW B VOLUME 41, NUMBER 2 15 JANUARY 1990-I

Observation of normal Hall coefficient of amorphous Si thin films prepared by low-pressure chemical-vapor deposition

N. Du, Y. T. Zhu, and B. Y. Tong
Department of Physics, University of Western Ontario, London, Ontario, Canada N6A 3K7

S. K. Wong
Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7
(Received 5 July 1989; revised manuscript received 20 October 1989)

Hall coefficients of the normal sign have been observed in doped amorphous silicon thin films fabricated by the low-pressure chemical-vapor deposition method. In phosphorous-doped material, the magnitude of the Hall mobility is 0.15 $cm^2V^{-1}s^{-1}$, corresponding to a room-temperature conductivity 0.3 $(\Omega\,cm)^{-1}$. In boron-doped amorphous silicon, the magnitude of the Hall mobility is 0.11 $cm^2V^{-1}s^{-1}$. The material is amorphous in structure as identified by various methods.

Early works of Hall-effect measurements on amorphous materials were concentrated on chalcogenide glasses (see review by Rollos,[1] and Fritzsche[2]). The measurements on amorphous silicon thin films (*a*-Si:H) fabricated by the glow discharge method have been made and reported by LeComber, Jones, and Spear,[3] Overhof and co-workers,[4,5] and by Dresner.[6] The common features of these measurements are (i) the magnitude of Hall mobility is small (between 10^{-2} to 10^{-1} $cm^2V^{-1}s^{-1}$) and increases slightly with measurement temperature; (ii) the well-known sign anomaly of the Hall coefficient, e.g., for *a*-Si:H thin films, the so-called "double reversal" phenomenon: the sign of Hall coefficient of both phosphorus- and boron-doped films are opposite to that of thermoelectric power. So far, no systematic measurements on low-pressure chemical-vapor deposition (LPCVD) amorphous (*a*-Si) thin films have been reported.

In this Rapid Communication we present Hall-effect measurement experiments on both P- and B-doped LPCVD *a*-Si thin films, and report, for the first time, the observation of a normal Hall coefficient in amorphous Si samples.

The thin film (2000 to 5000 Å) for Hall mobility measurement was deposited on Corning 7059 glass by the LPCVD method. We designed the Hall sample to be as small as it could be easily handled in order to compensate the possible inhomogeneity of the films and to reduce the misalignment voltage. The dimension of the sample was 0.953×3.175 mm^2. The sample pattern was realized by lithography to ensure better alignment of the probes. For electrodes, evaporated Cr was used as a first layer to make contact with the silicon thin film and then Au was deposited on top of Cr. It was then annealed to reduce contact noise. The sample was finally connected to the measurement circuits by indium solder. The sample chamber was made of stainless steel and operated under vacuum.

The Hall effect was investigated in a magnetic field of up to $B=1.5$ T (Varian V-3400) produced by a magnet which could be rotated. A value of $2V_H$ was obtained by reversing the direction of the magnetic field. Keithley 181 and Keithley 600B electrometers were used to record the Hall voltage. The output from the electrometers was directly connected to a microcomputer for storage and analysis.

The LPCVD system for Si thin-film deposition was described elsewhere.[7] The following conditions were used for film fabrication: substrate temperature T_s from 460 to 620 °C and a phosphine-silane (or diborane-silane) ratio from 1×10^{-5} to 1×10^{-2}. In this range, both amorphous and microcrystalline (μc) materials were obtained. The structure characterizations of our films were based upon: (i) x-ray diffraction, (ii) Raman spectroscopy,[8] (iii) TEM,[9] and (iv) electronic properties of the films.

All μc samples fabricated by LPCVD showed normal Hall sign while for amorphous samples Hall coefficients of both the normal and anomalous sign were observed. The normal Hall coefficient shown by the amorphous sample greatly interested us. In Fig. 1, we present two typical Hall-effect measurement results for phosphorus-doped *a*-Si samples No. 1 and No. 2 (parallel results are also available for boron-doped samples). Table I lists the parameters of samples 1 and 2. The magnitude of the normal Hall mobility (sample 2) is about 3 times higher than that of the anomalous Hall mobility (sample 1). In both phosphorus- and boron-doped materials, the magnitude of the observed mobility in anomalous samples is less than that of normal Hall samples.

It has been reported[9] and also was our observation that all μc-Si films have a normal Hall coefficient. An important question arises: Is sample 2 really an amorphous material? To answer this, extensive structure analysis was carried out. All the available structure analysis techniques confirmed that sample 2 was amorphous in structure. Figure 2 is the Raman scattering results for both samples 1 and 2, taken from the same sample used for the Hall measurement. For comparison, the spectra of *n*-type single crystal Si and LPCVD μc-Si films are also included in Fig. 2. The broad peaks of samples 2 and 1 around 475 cm^{-1} are typical amorphous Raman optical mode peaks. X-ray diffraction on sample 2 showed no crystallinity (Fig. 3). Transmission-electron microscopy on sample 2 revealed a typical amorphous diffraction pattern which is shown in Fig. 4.

Studies on transport properties also indicated that sam-

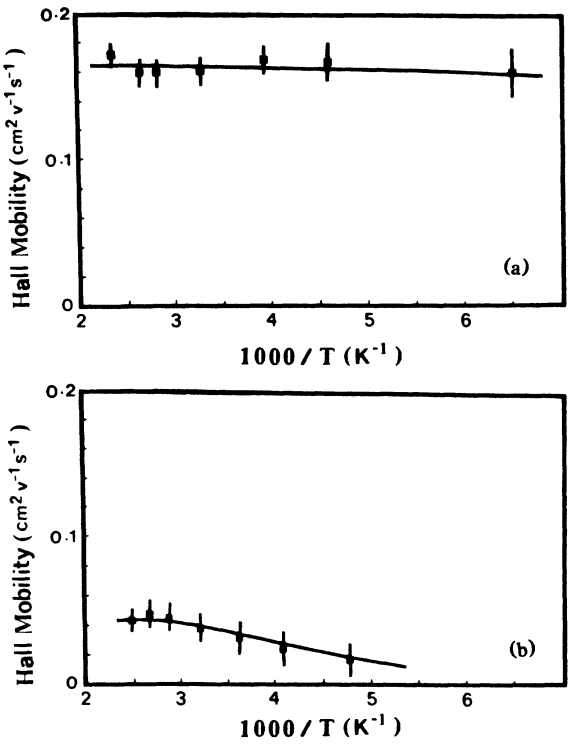

FIG. 1. Hall mobility of amorphous (a) sample No. 2, and (b) sample No. 1.

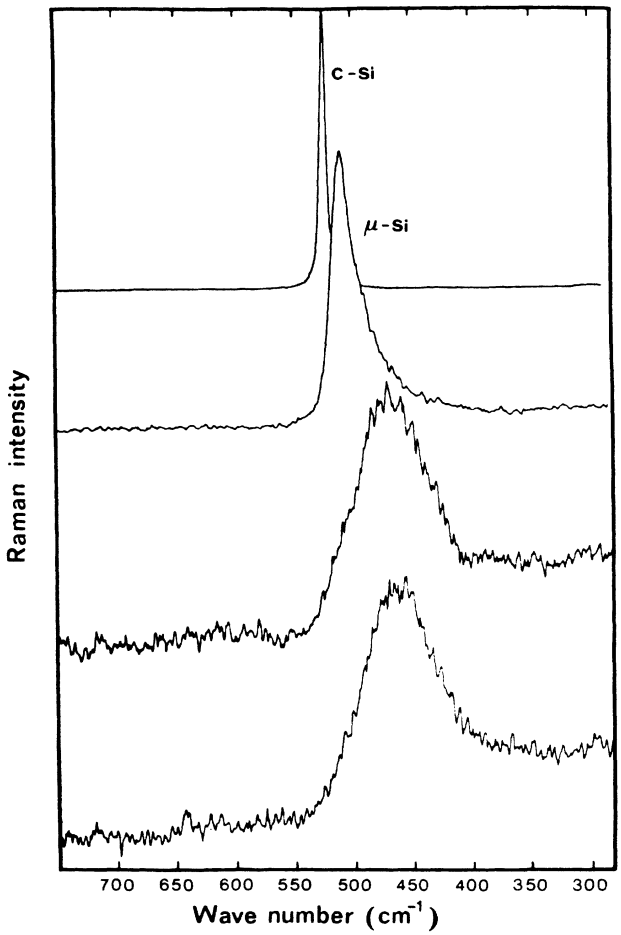

FIG. 2. Raman spectrum of single-, microcrystalline-, and amorphous-Si samples (No. 2 and No. 1).

ple 2 belonged to the amorphous, not to the μc family. For example, the conductivity of μc-Si under the same dopant gas ratio should be at least 2 to 3 orders of magnitude higher than that of sample 2. The temperature dependence of the Seebeck coefficient of sample 2 was typical of amorphous Si, and different from that of μc material.[10]

The magnitude of normal Hall mobility in boron-doped amorphous silicon sample 3 prepared from LPCVD was 0.11 $cm^2V^{-1}s^{-1}$, as compared to a value less than 0.05 $cm^2V^{-1}s^{-1}$ for a-Si of the abnormal sign (sample 4), and 4.9 $cm^2V^{-1}s^{-1}$ for μc-Si (sample 5).

We associate the normal Hall coefficient and high Hall mobility value of sample 2 with a random silicon network structure possessing good short-range order. In Table I, one notices that the solid-phase phosphorus concentration in sample 2 is substantially less than that of sample 1, but the dark conductivity of sample 2 at room temperature is 1 order of magnitude higher than that of sample 1. The conductivity (0.3 $\Omega^{-1}cm^{-1}$) of the LPCVD samples, e.g., sample 2 (normal Hall material), has the highest value reported so far among amorphous Si materials containing the same amount of dopant fabricated by various methods. It is, however, still 2 to 3 orders below that of μc-Si. High doping efficiency is an indication of good network structure.

Double reversal of the Hall constant is a ubiquitous feature of glow-discharge amorphous silicon (a-Si:H). Sign anomaly is accounted for by theoretical models[11-13] only in the limit of extreme strong localization in which the Ioffe criterion, i.e., localization length less than atomic spacing, is invoked. Even in this limit, the normal sign is not excluded. The sign is dependent on the ring statistics of the silicon network. If the continuous random network

TABLE I. Parameters of phosphorous-doped amorphous silicon thin-film samples No. 1 and No. 2.

	Sample 1	Sample 2
Gas ratio R	4×10^{-3}	1×10^{-3}
Substrate temperature T_s	540°C	560°C
P concentration in film S	4.8 atm%	1.31 atm%
Room-temperature conductivity σ	2×10^{-2} $(\Omega cm)^{-1}$	0.3 $(\Omega cm)^{-1}$
Hall mobility μ_H	0.04 cm^2/Vs	0.15 cm^2/Vs
Sign of the Hall coefficient	+	−

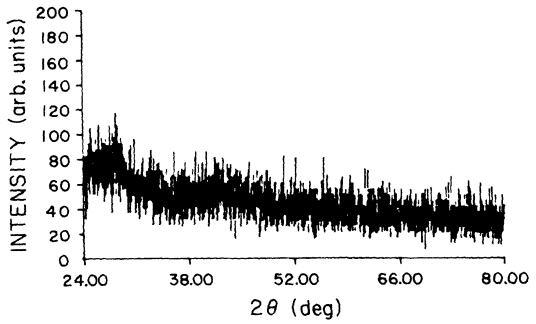

FIG. 3. X-ray diffraction pattern of sample 2.

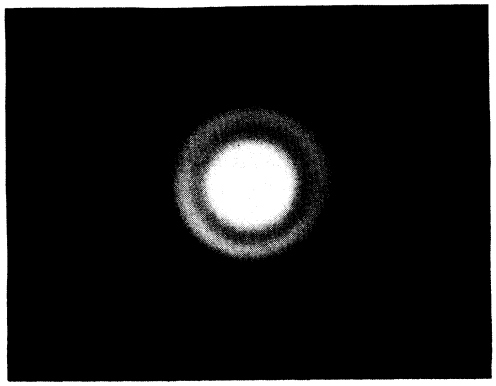

FIG. 4. TEM diffraction pattern of sample 2.

is taken as a model for the ideal amorphous silicon structure, six-member rings prevail,[14] and thus the sign should be normal according to the theory. It is surprising that the normal Hall effect has not been found in glow-discharge *a*-Si:H. The glow-discharge material is deposited in the presence of hydrogen, and the film contains more than 5 at.% of hydrogen. Hydrogen relieves stiffness in the structure,[15] and may have changed the ring statistics significantly. The ring statistics of a network model containing hydrogen has not been studied. By contrast, the LPCVD films contain much less hydrogen, the maximum amount observed being less than one-tenth of that in the glow-discharge material.

There are two classes of disorder that can cause localization in *a*-Si: topological structural disorder and random scattering centers such as defects and foreign atoms. If the continuous random network is taken as the ideal model of *a*-Si without hydrogen, the former alone is not likely to bring about the strong localization. Short-range local order in this model is well preserved.[16] Recent Raman studies on *a*-Si showed that the short-range order of amorphous material can be improved substantially by optimizing the fabrication conditions.[17] In our quest for amorphous specimens having the normal sign in the Hall coefficient, we aimed at minimizing the latter, including hydrogen. We carefully mapped out a wide range of the fabrication parameters in the LPCVD system. They can be translated into physical quantities such as concentration of dangling bonds, dopant, and hydrogen. These parameters are not mutually independent. For example, an increase in dopant concentration ($n < 10^{19}$ cm^{-3}) simultaneously reduces the amount of dangling bonds. Amorphous silicon with the normal sign is found only in a small region in the multidimensional parameter map.

One may raise the question of whether these samples are composed of microcrystals too small to be detected by x-ray diffraction, Raman spectroscopy, and TEM. We believe this is not so. In the parameter map, the region of producing the normal sign material lies almost totally within the amorphous realm. Only on the high substrate temperature side does it touch the μc-Si region. If we move from the normal region in the direction of either too much or too little dopant concentration, we end up on the abnormal amorphous region. Furthermore, physical properties of the normal sign material have characteristics distinctively different from those of the μc material (for example, the Seebeck coefficient). If the material is a composite of crystals of such small size as to escape detection, the amount of grain-boundary states must be overwhelmingly large.

In summary, we have observed the normal Hall coefficient in both P- and B-doped LPCVD *a*-Si thin films. They are produced only in a small region in the fabrication parameter map. We believe that this material which contains much less hydrogen as in *a*-Si:H has an improved network structure.

[1]M. Rollos, Philos, Mag. B **38**, 477 (1978).

[2]H. Fritzsche, in *Amorphous and Liquid Semiconductors,* edited by J. Tauc (Plenum, London, 1974), p. 221.

[3]P. G. LeComber, D. I. Jones, and W. E. Spear, Philos. Mag. **35**, 1173 (1977).

[4]W. Beyer, R. Fischer, and H. Overhof, Philos. Mag. B **39**, 205 (1979).

[5]H. Overhof, Philos. Mag. B **44**, 317 (1981).

[6]J. Dresner, Appl. Phys. Lett. **37**, 742 (1980).

[7]A. Berman, Z. M. Chen, K. P. Chik, P. K. John, P. K. Lim, A. Prasad, G. Strinivasan, B. Y. Tong, and S. K. Wong, J. Non-Cryst. Solids **59&60**, 751 (1983).

[8]S. T. Kshirsagar and J. S. Lannin, Phys. Rev. B **25**, 2916 (1982).

[9]G. Willeke, W. E. Spear, D. I. Jones, and P. G. LeComber, Philos. Mag. B **46**, 177 (1982).

[10]N. Du, Y. Zhu, K. P. Chik, P. K. John, S. K. Wong, and B. Y. Tong, J. Non-Cryst. Solids (to be published).

[11]L. Friedman, Philos. Mag. B **38**, 467 (1978).

[12]D. Emin, Philos. Mag. **35**, 1189 (1977).

[13]B. Movaghar, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritzsche, and S. R. Ovshinsky (Plenum, New York, 1985), pp. 399–412.

[14]In the continuous random network models, the statistics of the five-member rings range from 0% in the Connell-Temkin model, to 20% in the Polk model. See discussions in B. Y. Tong and F. C. Choo, Solid State Commun. **20**, 957 (1976); also see R. Grigorovici, in *Amorphous and Liquid Semiconductors,* edited by J. Tauc (Plenum, London, 1974), pp. 45–99.

[15]J. C. Knights, J. Non-Cryst. Solids **35&36**, 159 (1980).

[16]In the Polk model, the bond length is hardly changed at all, and the bond-angle deviation is about 9%; see D. E. Polk and D. S. Boudreau, Phys. Rev. Lett. **31**, 92 (1973).

[17]J. S. Lannin, N. Maley, and S. T. Kshirsagar, Solid State Commun. **53**, 939 (1985).

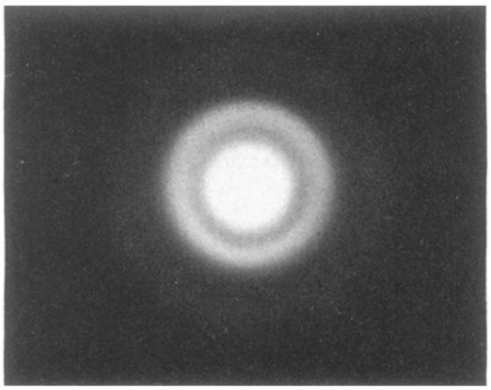

FIG. 4. TEM diffraction pattern of sample 2.