Thermally induced metastable defects in hydrogenated amorphous silicon and silicon-carbon alloy films

Xixiang Xu,* Akihisa Okumura, Akiharu Morimoto, Minoru Kumeda, and Tatsuo Shimizu
Department of Electronics, Faculty of Technology, Kanazawa University, Kanazawa 920, Japan
(Received 30 March 1988)

Thermally induced metastable defects in hydrogenated amorphous silicon (a-Si:H) and silicon-carbon alloy (a-Si$_{1-x}$C$_x$:H) films are studied by electron spin resonance (ESR) and conductivity measurements. We found that both undoped and P-doped a-Si$_{1-x}$C$_x$:H films exhibit thermal-equilibrium phenomena similar to those in a-Si:H although they have much higher defect densities. By heating the samples *in situ* during ESR measurements, we were able to directly observe the density of dangling bonds in both a-Si:H and a-Si$_{1-x}$C$_x$:H as the samples move from a frozen-in state into a temperature-dependent equilibrium. The influence of surface states and long-term drift of exposed surface on the thermal-equilibrium process has also been extensively investigated.

I. INTRODUCTION

It has recently been suggested that hydrogenated amorphous silicon (a-Si:H) can reach some sort of thermal equilibrium above a characteristic temperature, i.e., so-called thermal-equilibrium temperature, T_e. Smith and Wagner first investigated the intrinsic dangling bond density in undoped a-Si:H and suggested that the recombination of thermally generated carriers creates defects at high temperature which are frozen in by normal cooling rates.[1-3] Several pieces of experimental evidence have been reported on the thermal-equilibrium defects in undoped, phosphorus-doped, and boron-doped a-Si:H.[3-10] Focused mainly on the B- or P-doped a-Si:H, Street *et al.* investigated the thermal-equilibrium processes by conductivity, sweep out, hydrogen diffusion, and electron spin resonance (ESR) measurements. In their hydrogen-glass model, Street *et al.* first described the association between the equilibration of defects and the diffusion of hydrogen bonded to silicon.[4] They proposed that the motion of hydrogen from site to site and its insertion into weak Si—Si bonds is the dominant mechanism by which thermal equilibrium is established. Smith *et al.* suggested that, in undoped a-Si:H above T_e, defects are in a thermal-equilibrium state and the density of defects is thermally activated. Previous reports have inferred the defect density at high temperatures by performing room-temperature measurements before and after quenching. Therefore, the origin of the thermally induced defects has not yet been definitely clarified, especially in undoped a-Si:H. Furthermore, there have been few reports on the thermal-equilibrium process in hydrogenated amorphous Si-based alloys such as hydrogenated amorphous silicon-carbon alloy (a-Si$_{1-x}$C$_x$:H).

Thermally induced metastable defects in a-Si$_{1-x}$C$_x$:H were detected for the first time by ESR and conductivity measurements in the present work. Preliminary results were already published.[11] From the annealing-temperature- (T_A-) dependent density of dangling bonds after fast cooling (10 °C/s) measured by ESR, we found that equilibrium temperature T_e varies with carbon content in a-Si$_{1-x}$C$_x$:H. In the temperature-dependent dark-conductivity measurements, it was found that thermally induced effects in P-doped a-Si:H and P-doped a-Si$_{1-x}$C$_x$:H are influenced both by doping level and C content.

By measuring the temperature dependence of the density of dangling bonds by ESR, we observed the increase in the density of dangling bonds above T_e both for a-Si:H and a-Si$_{1-x}$C$_x$:H. This result should provide the first direct evidence of the thermal-equilibrium process in these materials.

II. EXPERIMENT

The a-Si$_{1-x}$C$_x$:H films used in this study were prepared by rf glow discharge (GD) of undiluted SiH$_4$ and CH$_4$. PH$_3$ was used as a dopant gas. The rf power and substrate temperature were 10 W and 350 °C for a-Si$_{1-x}$C$_x$:H deposition (20 W and 350 °C for a-Si:H deposition). Fused quartz was used as the substrate for both ESR and conductivity measurements except when otherwise specified. The film thickness was 2–3 μm. ESR measurements were carried out mainly at room temperature by an X-band Varian E109 system. CuSO$_4$·5H$_2$O was used as a standard for calibrating the spin density.

Annealing was performed in vacuum (2×10^{-5} torr). Fast cooling (FC) was accomplished by breaking vacuum and quickly dropping the sample into liquid N$_2$. The average cooling rate in this method was estimated to be larger than 10 °C/s. The slow cooling (SC) was achieved by an automatically controlled cooling procedure and a typical rate was 0.04 °C/s. Both fast cooling and slow cooling were carried out after a 30-min annealing in vacuum.

III. RESULTS AND DISCUSSION

A. Thermally induced defects in undoped a-Si:H and a-Si$_{1-x}$C$_x$:H

The thermally induced-increase of spin densities N_s in undoped a-Si:H measured by ESR is plotted as a function
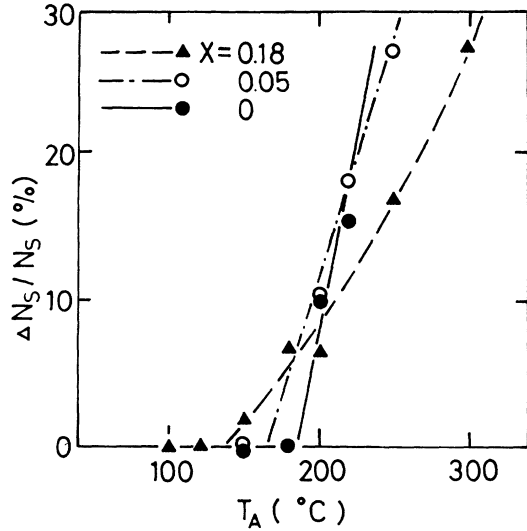
FIG. 1. Thermally induced relative increase of spin densities in undoped $a\text{-Si}_{1-x}C_x\text{:H}$ films measured by ESR vs annealing temperature T_A. ΔN_s is the difference in the spin densities for films after fast cooling and after slow cooling, and N_s is the spin density for films after slow cooling.

of annealing temperature T_A in Fig. 1. The ESR signals are believed to originate from dangling bonds in these films. In the region of T_A from 120 to 180 °C, no difference was observed in a-Si:H within the ESR-measurement precision between fast-cooling and slow-cooling treatments. But fast coolings both from 200 and 220 °C really make the spin density N_s increase remarkably, with increases of 1.6×10^{15} cm^{-3} for 200 °C and 2.6×10^{15} cm^{-3} for 220 °C fast cooling. We can say that there exists a critical temperature, i.e., a temperature at which the defect density moves to its thermal-equilibrium value on a time scale of a few minutes, T_e between 180 and 200 °C, which is consistent with the value obtained from the photoconductivity measurement by McMahon and Tsu.[8] Compared with the initial magnitude of the effective bulk spin density (the spin density per unit volume including both surface and bulk spin density), 200 and 220 °C fast cooling induced 10% and 17% increments, respectively. If, however, we assume that the thermally induced spin density is mainly contributed by bulk defects, it is probably more reasonable to compare a relative increase in the spin density with the bulk spin density, which means that the fast cooling from above T_e almost doubled the bulk spin density in a-Si:H because more than half of the spin density is expected to arise from the surface defects.[12]

ESR measurements were performed on an a-Si:H film coated with a thin a-Ge:H layer to suppress the effect of surface states. a-Ge:H was used because the broad ESR signal from Ge dangling bonds can easily be distinguished from the narrow ESR signal from Si dangling bonds. A 500-Å-thick a-Ge:H coating layer was deposited by decomposing $GeF_4 + H_2$ on 2-μm-thick a-Si:H deposited on the fused-quartz substrate. Therefore, there is no free

surface of a-Si:H, but a new interface between a-Si:H and a-Ge:H is added. From the a-Si:H/a-Ge:H multilayers (with 11 100-Å-thick a-Ge:H and 10 200-Å-thick a-Si:H sublayers), the interface layer was estimated to provide the interface defects less than 1.0×10^{11} spins/cm^2, much smaller than the density of surface states in a-Si:H with free surface (about 1.4×10^{12} cm^{-2}). The sequence of changes in the spin density for this sample upon thermal treatments and storage time in air at room temperature is shown in Fig. 2. The measurement started with the sample kept in air for about one month after deposition. Spin densities in Fig. 2 are normalized to this initial value. Then the sample was annealed at 210 °C for 30 min and fast cooled (first quench). As shown in Fig. 2, about 10% of the increase in the spin density occurred after 210 °C fast cooling and five-day resting at room temperature induced some relaxation (a decrease of about 15% in N_s). Slow cooling after annealing at 210 °C made the spin density decrease further. Lastly, this sample was quenched from 210 °C (second quench), which causes N_s to increase again, though not recovering exactly to the same value after the first FC (the decrease in N_s from the second-quench process compared with the first-quench process might be due to some irreversible change in the sample). Therefore, we can see that 210 °C quench for this a-Si:H sample induces a relative increase of 30–45 % in the spin density, which is larger than that shown in Fig. 1 for a-Si:H without an a-Ge:H coating layer. From this experiment, we can see that as the influence of surface defects is reduced, the relative increase in the total defect density is enhanced.

Extension of this study to $a\text{-Si}_{1-x}C_x\text{:H}$ films shows that the alloying of a-Si:H with carbon alters the thermally induced effects. T_A dependence of a relative increase in the spin density N_S for $a\text{-Si}_{1-x}C_x\text{:H}$ films with $x = 0.05$ and 0.18 are also shown in Fig. 1. Here two points are worth noting. One is that T_e, if the data can still be interpreted in terms of a thermal-equilibrium process, varies with C content. Another point is that the slope of a relative increase in the density of dangling bonds with T_A decreases with an increase in C content. For the first
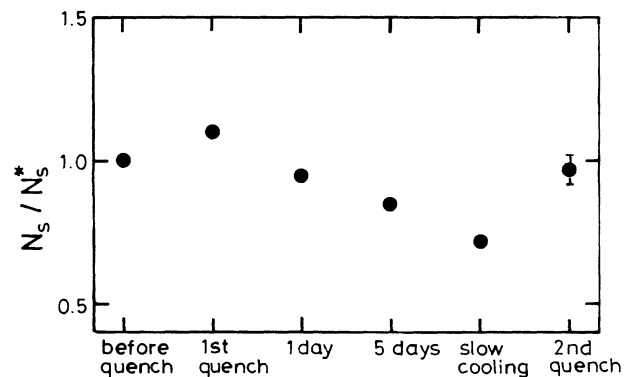

FIG. 2. Spin densities of a-Si:H coated with an a-Ge:H layer after various thermal treatments. N_s is normalized to N_s^*, the spin density measured before the first quench.

point, whether T_e decreases or increases with an increase in C content depends on the method in which T_e is determined. If we extrapolate the relative increase in the spin density to zero to define $T_e(0\%)$, $T_e(0\%)$ decreases from about 190 °C for a-Si:H to around 150 °C for a-Si$_{0.82}$C$_{0.18}$:H. In another way, we may define T_e as the temperature from which fast cooling will induce a certain amount of ΔN_s, for example, 20% of a relative increase, resulting in $T_e(20\%)$. As shown in Fig. 3, the trend of variation of $T_e(20\%)$ is very different from that of $T_e(0\%)$ upon C content, $T_e(20\%)$ increasing from 220 °C for a-Si:H to about 260 °C for a-Si$_{0.82}$C$_{0.18}$:H.

Probably it is more physically reasonable to expect that alloying carbon in a-Si:H will increase rather than decrease the thermal-equilibrium temperature T_e. Compared with a-Si:H, a-Si$_{1-x}$C$_x$:H alloys have a larger H content, many more dangling bonds, and stronger bonding energy for hydrogen.[13] If, in a-Si$_{1-x}$C$_x$:H alloys, the role of the far larger amounts of H atoms and dangling bonds overpowers the increase in the bonding energy of H on the diffusion coefficient, it is possible for a-Si$_{1-x}$C$_x$:H alloys to have a lower equilibrium temperature than a-Si:H. Recently, Matsuo *et al.* have observed that T_e drops as H content increases in P-doped a-Si:H.[9] But increasing C content in alloy films will introduce inhomogeneous structure and make the diffusion coefficient of H distributed, which can explain the experimental result that the slope of a relative increase in the density of dangling bonds with T_A decreases with C content in a-Si$_{1-x}$C$_x$:H.

B. Conductivity of P-doped a-Si:H and a-Si$_{1-x}$C$_x$:H

For P-doped a-Si:H, it has been found that the temperature-dependent dark conductivities below equilibrium temperature T_e are quite different after thermal treatments. The conductivity measured at temperature below T_e is enhanced by fast quenching from temperatures well above T_e, and this conductivity enhancement slowly relaxes away. Above T_e, different conductivity curves converge to a single set of values which are independent of thermal treatments. These results were taken as a signature of the thermal equilibration in P-doped a-Si:H by Street *et al.*[4] If the thermal equilibration can occur in a-Si$_{1-x}$C$_x$:H (at least in those with moderate C contents, e.g., $x=0.2$), it is expected that a similar phenomenon will be observed in conductivity measurements.

In fact, we have observed such a phenomenon for P-doped a-Si$_{1-x}$C$_x$:H films with various amounts of C content in temperature-dependent conductivity measurements. The doping gas ratio of PH$_3$ to SiH$_4$+CH$_4$ is kept constant at 5×10^{-3} and the C contents range from 3 to 27 at. %. Optical band gaps E_{opt} and activation energies E_a above T_e and below T_e after fast cooling (10 °C/sec) are listed in Table I. Figure 4 shows the temperature dependence of the dark conductivities for a-Si$_{1-x}$C$_x$:H samples with $x=0$, 0.07, and 0.27. In the temperature region below T_e, fast cooling makes the conductivity increase while slow cooling makes the conductivity decrease compared with the conductivity in the as-
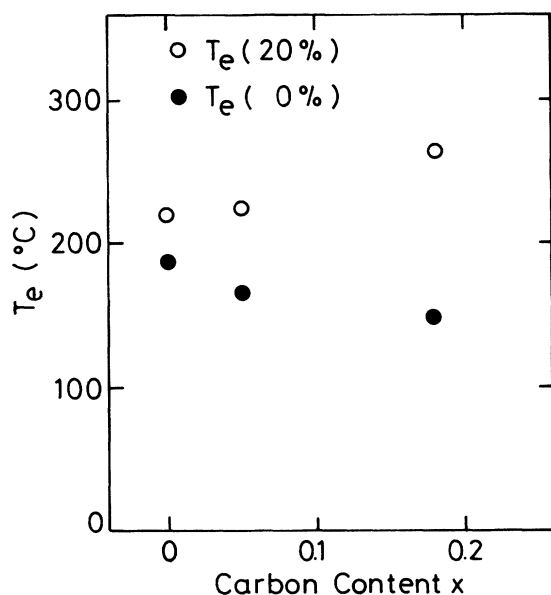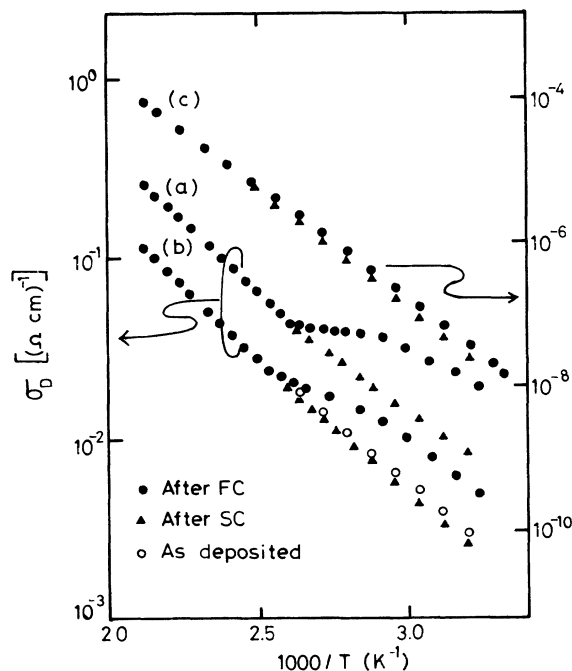

FIG. 3. Two kinds of carbon-content-dependent thermal-equilibrium temperatures determined from Fig. 1. $T_e(0)$ is the temperature to which ΔN_s is extrapolated to 0. $T_e(20\%)$ is the temperature from which FC will induce 20% of a relative increase in the spin density.

FIG. 4. Temperature dependence of the dark conductivity in P-doped a-Si$_{1-x}$C$_x$:H films. The doping gas ratio is kept at 5×10^{-3}, and the carbon contents x for (a), (b), and (c) are 0, 0.07, and 0.27, respectively.

TABLE I. Optical band gap E_{opt} and activation energy E_a above T_e and below T_e after fast cooling for a-Si$_{1-x}$C$_x$:H in units of eV.

	$x=0$	$x=0.03$	$x=0.07$	$x=0.17$	$x=0.27$
E_{opt}	1.66	1.69	1.70	1.90	2.02
E_a, $T > T_e$	0.29	0.32	0.34	0.54	0.65
E_a, $T < T_e$	0.19	0.23	0.25	0.51	0.62

deposited state. The results for a-Si$_{0.93}$C$_{0.07}$:H are shown in Fig. 4. The equilibration temperature T_e can be determined to be around 120 °C for this sample.

The increase in C content in a-Si$_{1-x}$C$_x$:H is found to reduce the change due to fast cooling and to increase T_e. As shown in Fig. 4, the incorporation of 7 at. % C makes the relative increase in the conductivity below T_e induced by fast cooling smaller and T_e shift somewhat to a higher temperature, from 112 to 120 °C. The incoporation of 17 and 27 at. % C further reduces the change due to fast cooling, making T_e shift to around 130 °C.

For the origin of the thermally induced conductivity in a-Si$_{1-x}$C$_x$:H, especially its trend of the change with C content, there are at least two possibilities. One is that the increment of C content makes it difficult to reach thermal equilibration in P-doped a-Si$_{1-x}$C$_x$:H, which will be expected to increase T_e. The other is that the introduction of carbon will change the doping efficiency of P although the doping gas ratio remains unchanged.

To see if the doping level influences the thermally induced conductivity, similar temperature-dependent dark-conductivity measurements were carried out on three P-doped a-Si:H films with different doping gas ratios after fast cooling from 250 °C. Figure 5 shows that as
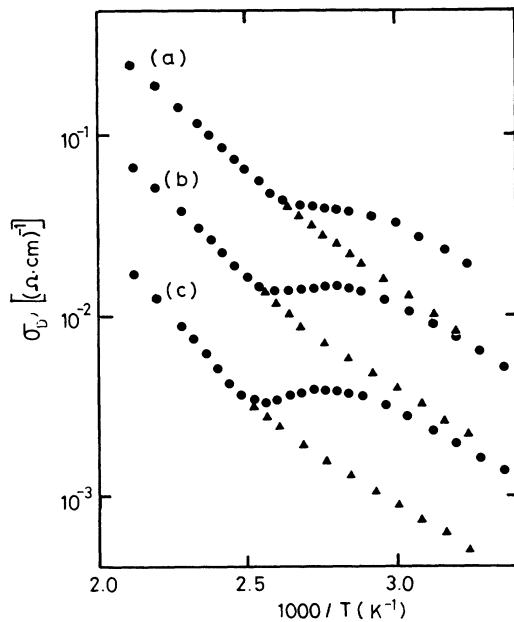
the doping gas ratio decreases from 5×10^{-3} to 2.7×10^{-5}, T_e shifts from 112 to 127 °C. The decrease in T_e with doping gas ratio for P-doped a-Si:H can be explained by the H-glass model because the hydrogen diffusion coefficient increases as a doping level increases,[4] which will make it possible for the defects to equilibrate through the motion of hydrogen atoms at lower temperature.

C. Temperature-dependence measurement of the spin density in a-Si:H and a-Si$_{1-x}$C$_x$:H

If thermal equilibration occurs in a-Si$_{1-x}$C$_x$:H alloy films, an increase in the ESR spin density should be observed above T_e.

ESR measurements at various temperatures from room temperature (RT) to about 250 °C were carried out both for the film on the fused quartz and the flake samples of a-Si$_{0.8}$C$_{0.2}$:H and a-Si:H. The flake samples were prepared by removing the Al substrate in dilute HCl solution. The measurement temperature is controlled by a JES-VT-3A variable temperature controller (Japan Electron Optics Laboratory Co. Ltd.). Because a small irreversible decrease in the spin density occurs in the first increasing temperature procedure, the sample was first heated to about 250 °C in air and held there for more than 1 h. Then the ESR data were taken by gradually decreasing the temperature from 250 °C to RT. These data were ascertained to agree well with those taken in a subsequent experiment in which the temperature was gradually scanned upward. In every step of the measurement, the sample was held at the measurement temperature for about 20 min to reach a thermal uniformity before ESR measurements. The ESR marker (Mn^{2+} in MgO powders) in the sample tube was also heated simultaneously to check the change in the Q value of the cavity. The intensity of the ESR signal should be proportional to $N_s(T)/T$ in the temperature range above RT. Here $N_s(T)$ designates the temperature-dependent spin density. The spin density of the marker was assumed to be independent of temperature. The temperature dependence of the spin density $N_s(T)$ for a-Si:H and a-Si$_{0.8}$C$_{0.2}$:H determined in this way are shown in Fig. 6. $N_s(T)$ is normalized to those at room temperature. No obvious differences were found between the results of the film on the fused quartz and the flake samples. As the temperature increases, the spin density of a-Si$_{0.8}$C$_{0.2}$:H remains unchanged up to about 100 °, and beyond that temperature it shows a gradual increase. The spin density measured at 250 °C, $N_s(250 °C)$, shows an increase of about 40%, which is consistent with the result shown in Fig. 1
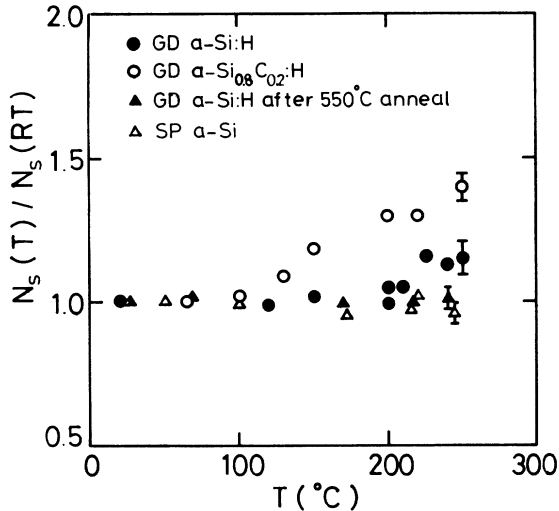

FIG. 5. Temperature dependence of the dark conductivity in P-doped a-Si:H films. Doping gas ratios are (a) 5×10^{-3}, (b) 2.7×10^{-4}, and (c) 2.7×10^{-5}. Circles show the results measured after FC and triangles show those measured after SC.

FIG. 6. Temperature dependence of the spin density $N_s(T)$ for a-Si:H, a-Si$_{0.8}$C$_{0.2}$:H, a-Si:H annealed at 550 °C, and a-Si. $N_s(T)$ are normalized to the values measured at room temperature N_s(RT), 1.0×10^{16} cm^{-3} (a-Si:H), 0.9×10^{18} cm^{-3} (a-Si$_{0.8}$C$_{0.2}$:H), 2.4×10^{18} cm^{-3} (a-Si:H after 550 °C anneal), and 2×10^{20} cm^{-3} (SP a-Si).

where the fast cooling from 250 °C introduced about a 20% increase of frozen-in defects. For a-Si:H, no obvious increase is observed up to about 200 °C, but a relative increase of 10–20 °% appears at 220 and 245 °C (see Fig. 6). A problem for a-Si:H, however, is that the accuracy was not as good as that for a-Si$_{0.8}$C$_{0.2}$:H because a-Si:H has a much lower spin density than a-Si$_{0.8}$C$_{0.2}$:H.

In order to see whether H atoms in the film are essential for the thermal equilibration of defects, we measured the temperature dependence of the spin density also for a-Si:H annealed at 550 °C for more than 90 min and a-Si without H prepared by magnetron sputtering (SP a-Si). The annealed a-Si:H has a very small amount of H, less than 1 at. % estimated from infrared absorption measurement. For these two kinds of samples, no obvious change of the spin density with temperature was observed up to about 250 °C as shown in Fig. 6. At present, we cannot exclude the possibility that there may be T_e above 250 °C for them, but at least we can say that H plays a very important role in the thermal-equilibrium process. It should be mentioned that the linewidth of the ESR signal increased remarkably with increasing temperature for a-Si with a high spin density of about 10^{20} cm^{-3} although it does not appreciably change for other samples.

We believe that the present results provide the first direct evidence for the thermal equilibration of the spin density both in a-Si:H and a-Si$_{1-x}$C$_x$:H films. It should be noted that films without H or with a reduced H content do not exhibit the thermal equilibration of the spin density up to 250 °C.

D. Surface influence in ESR measurements

For undoped a-Si:H films, the spin density measured by ESR consists of two parts—bulk defects and surface de-

fects. From the observed thickness dependence of the spin density, bulk and surface spin densities have been determined to be about 2×10^{15} cm^{-3} and 1.4×10^{12} cm^{-2}, respectively,[12] which means that even for 5-μm-thick a-Si:H, the contribution from the surface to the effective bulk spin density is still larger than 50%. Smith et al. have measured thermal-equilibrium defects in undoped a-Si:H by means of constant photocurrent method (CPM), photothermal deflection spectroscopy (PDS), and ESR.[2] They found that relative changes in the total number of dangling bonds after fast cooling from 300 °C measured by ESR fall somewhere between relative changes measured by CPM (bulk defect) and PDS (bulk plus surface defect). However, for a-Si$_{1-x}$C$_x$:H films, a relative contribution from surface states to the total defect density becomes less important because the bulk spin density increases remarkably as C content increases, e.g., for the 1-μm-thick a-Si$_{0.8}$C$_{0.2}$:H film, more than 90% of spins are contributed by bulk defects. Therefore, we focus our attention here only on the change of the spin density in a-Si:H films with different surface states after thermal treatments.

ESR measurements were made on the undoped a-Si:H films with various surface conditions after fast cooling from 210 °C which include fresh surface (newly deposited sample), surface with naturally oxidized layer (several months exposure to air after deposition), surface treated by HF etching (most of the oxidized layer was etched off), and a-Ge:H–coated surface (a-Si:H without free surface). Relative changes of the spin density after 210 °C fast cooling are plotted against a storage time in air at room temperature in Fig. 7. It is shown that relative changes of the spin density versus a storage time are influenced by surface conditions. For the HF-etched sample, the spin density increases with a storage time and tends to saturate after about two weeks. This increase is believed to arise from the increase in the surface defects caused by surface oxidization. Similar data obtained by Lee et al.[14]
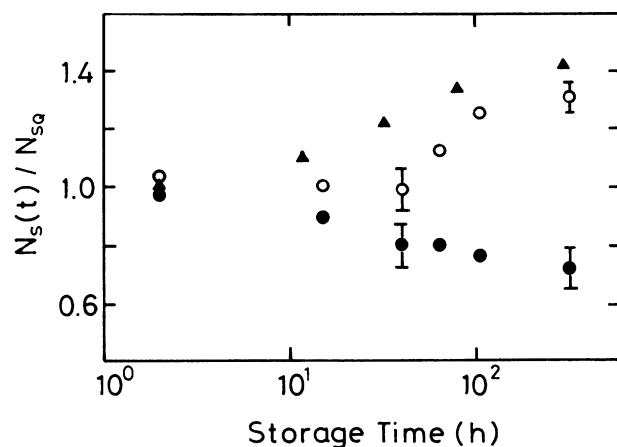

FIG. 7. Spin densities $N_s(T)$ normalized to that measured after fast quench from 210 °C N_{SQ} vs the storage time. Open and solid circles are, respectively, for a-Si:H after HF etching and a-Si:H coated with an a-Ge:H layer. Triangles show the data obtained by Lee et al. after Ref. 4.

are also shown in Fig. 7 for comparison. They found that the spin density grew with a storage time after fast cooling (1000 °C/s) from 210 °C. For the a-Ge:H–coated sample, however, the spin density decreases monotonically upon a storage time in air. In this case, the spin-density increase due to surface oxidization is avoided and the decrease in the spin density should originate from a relaxation toward a thermal equilibrium at room temperature. A qualitive similarity of data by Lee *et al.* to our data for the HF-etched sample suggests that the increase in the surface defects with a storage time might be the origin of the increase in the spin density for their case, but we cannot exclude other possibilities for the origin.

IV. CONCLUSION

Thermally induced defects in undoped and P-doped a-Si$_{1-x}$C$_x$:H were detected by ESR and conductivity mea-surements. Both undoped and P-doped a-Si$_{1-x}$C$_x$:H films exhibit thermal-equilibrium phenomena similar to those in a-Si:H although the alloying C content influences the value of T_e and the relative change of thermally in-duced defects. An increase in the density of dangling bonds above T_e for both a-Si:H and a-Si$_{1-x}$C$_x$:H was found by ESR measurement above room temperature, which provides the most direct evidence yet observed of the thermal equilibration of defects in these films.

ACKNOWLEDGMENTS

*On leave from Department of Physics, Lanzhou University, Lanzhou, Gansu, China.

[1]Z. E. Smith and S. Wagner, Phys. Rev. B **32**, 5510 (1985).

[2]Z. E. Smith, S. Aljishi, D. Slobodin, V. Chu, S. Wagner, P. M. Lenahan, R. R. Arya, and M. S. Bennett, Phys. Rev. Lett. **57**, 2450 (1986).

[3]Z. E. Smith and S. Wagner, Phys. Rev. Lett. **59**, 688 (1987).

[4]R. A. Street, J. Kakalios, C. C. Tsai, and T. M. Hayes, Phys. Rev. B **35**, 1316 (1987).

[5]M. Stutzmann, Phys. Rev. B **35**, 9735 (1987).

[6]R. A. Street, C. C. Tsai, J. Kakalios, and W. B. Jackson, Philos. Mag. B **56**, 305 (1987).

[7]X. M. Deng and H. Fritzsche, Phys. Rev. B **36**, 9378 (1987).

[8]T. J. McMahon and R. Tsu, Appl. Phys. Lett. **41**, 412 (1987).

[9]S. Matsuo, H. Nasu, C. Akamatsu, R. Hayashi, T. Imura, and Y. Osaka, Jpn. J. Appl. Phys. **27**, L132 (1988).

[10]S. C. Agawal, J. S. Payson, and S. Guha, Phys. Rev. B **36**, 9348 (1987).

[11]Xixiang Xu, Akiharu Morimoto, Minoru Kumeda, and Tatsuo Shimizu, Appl. Phys. Lett. **52**, 622 (1988).

[12]Xixiang Xu, Akiharu Morimoto, Minoru Kumeda, and Tatsuo Shimizu, Jpn. J. Appl. Phys. **26**, L1818 (1987).

[13]A. Morimoto, T. Miura, M. Kumeda, and T. Shimizu, J. Appl. Phys. **53**, 7299 (1982).

[14]C. Lee, W. D. Ohlsen, and P. C. Taylor, Phys. Rev. B **36**, 2965 (1987).