

SERI/STR-211-2393
DE84013038

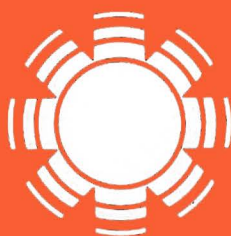
July 1984

Studies of Hydrogenated Amorphous Silicon

A Contract Report

S. G. Bishop
W. E. Carlos
Naval Research Laboratory

Yearly Report of
Contract No. DE-AI02-80C583116



SERI

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Operated for the

U.S. Department of Energy

under Contract No. DE-AC02-83CH10093

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:
Microfiche A01
Printed Copy A03

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SERI/STR-211-2393
UC Category: 63
DE84013038

Studies of Hydrogenated Amorphous Silicon

A Contract Report

S. G. Bishop
W. E. Carlos
Naval Research Laboratory

Yearly Report of
Contract No. DE-AI02-80C583116

July 1984

Prepared through an interagency
agreement for the Departments
of Energy and Defense of the
United States of America

SERI Technical Monitor: Amir Mikhail

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Prepared for the
U.S. Department of Energy
Contract No. DE-AC02-83CH10093

SUMMARY

Objective

To report on the results of probing the defect structure and bonding of hydrogenated amorphous silicon films using both nuclear magnetic resonance (NMR) and electron spin resonance (ESR).

Discussion

The doping efficiency of boron in a-Si:H was found to be less than 1%, with 90% of the boron in a threefold coordinated state. On the other hand, phosphorus NMR chemical shift measurements yielded a ratio of threefold to fourfold P sites of roughly four to one. Various resonance lines were observed in heavily boron- and phosphorus-doped films and a-SiC:H alloys. These lines were attributed to band tail states on twofold coordinated silicon. In a-SiC:H films, a strong resonance was attributed to dangling bonds on carbon atoms. ESR measurements on low-pressure chemical-vapor-deposited (LPCVD) a-Si:H were performed on samples provided by Chronar Corporation and by the University of Delaware. The defect density in the bulk of the films was 10^{17} /cc with a factor of three increase at the surface of the sample. The ESR spectrum of LPCVD-prepared films was not affected by prolonged exposure to strong light. However, it should be noted that these samples have 10^{17} spins per cc, while good glow discharge films have only 10^{15} spins per cc. Microcrystalline silicon samples provided by Brookhaven National Laboratory were also examined. The phosphorus-doped films showed a strong signal from the crystalline material and no resonance from the amorphous matrix. This shows that phosphorus is incorporated in the crystals and is active as a dopant. No signal was recorded from boron-doped films, which indicates that boron is also incorporated in the crystals.

1.0 Introduction

As in the case of crystalline semiconductors, the incorporation of group III elements such as boron into hydrogenated amorphous silicon (a-Si:H) produces p-type doping. Unlike the crystalline case, the doping efficiency in a-Si:H is quite low and therefore relatively large amounts of boron must be incorporated into the a-Si:H to achieve the desired results. One major purpose of the present contract is therefore to characterize the local structural environment of boron using NMR.

A second significant problem addressed during the past year has been the role of intrinsic and extrinsic defects in these films. For this work ESR has been the primary probe and in the past year films grown by both glow discharge and CVD have been studied.

A final objective of the present work has been to study dopants in microcrystalline films with an eye to learning what fraction of the dopant atoms (phosphorous or boron) reside in the microcrystals and what fraction reside in the amorphous matrix.

The objectives of this contract as outlined in the most recent work statement are as follows:

- 1) Perform magnetic resonance experiments on amorphous silicon films.
- 2) Use ESR to study light induced defects in amorphous silicon films.
- 3) Perform ESR measurements on microcrystalline films.

The research work of this contract has resulted in three publications (appendixes A-C and ref. 1-3) as well as several presentations at scientific meetings. The following section contains excerpts of the research accomplishments during the contract year for which details are available in the Appendixes.

The films used in this work have been obtained from RCA (D.E. Carlson and J. Dressner), Brookhaven National Laboratory (P. Vanier), IBM (J.A. Reimer), Chronar (A. Delahoy and F. Ellis) and the University of Delaware (R. Rocheleau).

2.0 Fulfillment of Contract Tasks

Task 1.1. Magnetic Resonance Measurements

Both NMR and ESR have been used to probe the defect structure and bonding in amorphous silicon films. Published work has included ^{11}B NMR studies of doped films^{1,2} (see Appendixes A and B) and ESR studies of carbon impurities³ (see Appendix C). In addition work has been done on depth profiling of centers in CVD films.

A. ^{11}B NMR Measurements

The doping efficiency of boron in a-Si:H is typically less than 1%. The high concentration of dopants required leads to the possible existence of mid-gap states associated with nonsubstitutional impurities.^{4,5} Other undesirable phenomena possibly linked with doping include changes in morphology and hydrogen distribution,^{6,7} and gap-narrowing attributable to a decrease in the bonded H content of the a-Si:H network.⁸ Recent optical absorption measurements of heavily B-doped (1 at.%) a-Si:H revealed an anomalously high absorption coefficient which was related to changes in texture and even mechanical stability of the films.⁹ In addition, cluster calculations of threefold-coordinated B in a-Si:H yielded energies that produce states in the gap while other trivalent Group-III elements were shown to be electronically passive.¹⁰

Knowledge of the local chemical environment of the dopant atoms in a-Si:H should provide a framework for the discussion of the electronic and optical properties attributable to the presence of large amounts of boron at nonsubstitutional sites. EXAFS studies of 1% As-doped a-Si:H showed that only

20±10% of the As atoms were fourfold-coordinated,¹¹ and ³¹P NMR chemical shift measurements yielded a ratio of threefold to fourfold P sites of roughly 4 to 1 in samples containing similar concentrations of P.¹² Previously reported ¹¹B NMR quadrupole-broadened linewidths in heavily B-doped (10 at.%) a-Si:H (provided by RCA) were consistent with threefold coordination of at least 90% of the ¹¹B nuclei.¹³ In the current work we have looked at films containing much less boron (0.7 at.); one of which also contained 0.6 at.% phosphorous, provided by Brookhaven National Laboratory (BNL). The uncompensated sample was provided by IBM.

In our original work on the highly doped material two NMR lines were seen. Fig. 1 compares the spin echo (essentially the Fourier transform of the line shape) for that sample with results obtained for the more lightly doped material. The RCA sample has a two component echo with characteristic times, T_2^* , at 61 MHz of ~13 μ sec and ~20 μ sec. However the more lightly doped IBM sample shows only one line with T_2^* ~20 μ sec. Similar results are obtained for the BNL sample.

The magnitude of the quadrupole interaction observed in a-Si(H,B) provides convincing evidence that the ¹¹B nuclei (~90% of the ¹¹B in the samples) giving rise to the observed linewidths are not tetrahedrally coordinated. For example, the ¹¹B linewidth in crystalline Si:B is <2 kHz¹⁴ in accord with the tetrahedral symmetry of the acceptor atoms; and, in borate minerals the ¹¹B quadrupole coupling constant, e^2qQ/h , is always found to be <0.9 MHz when the boron is four-coordinated and >2.4 MHz when it is three-coordinated regardless of the asymmetry of the nearest neighbor bonding.¹⁵

The boron sites in the RCA sample have been tentatively identified as a boron atom bonded to three silicon atoms (BSi₃) corresponding to the broad line ($e^2qQ/h=5.8$ MHz) and a boron atom bonded to two silicon atoms and a

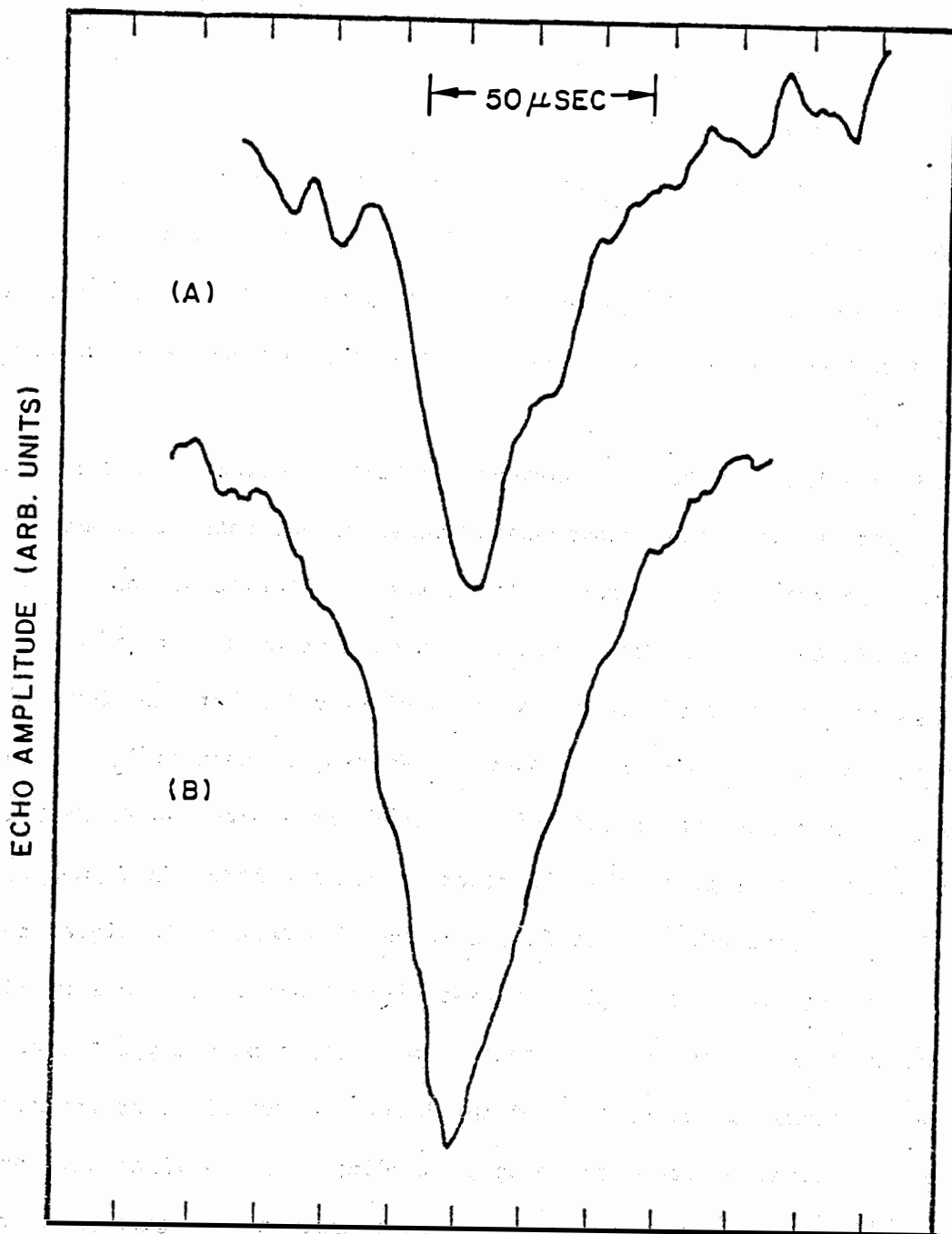


Fig. 1. Spin-echo signal of a) RCA at $\nu_0=61$ MHz; b) IBM at $\nu_0=60$ MHz

hydrogen atom (Si_2BH) or possibly bonded to two hydrogen atoms and one silicon atom (SiBH_2) for the narrow line ($e^2qQ/h=3.5$ MHz).¹³ We conclude that the linewidths of the IBM and the BNL samples are consistent with the presence of Si_2BH or SiBH_2 units in both materials.

Fig. 2 lends further support to the site assignments. The IBM sample was annealed at 550°C resulting in removal of $\sim 75\%$ of the hydrogen from the film. The width of the echo is seen to decrease from ~ 20 μsec to about ~ 12 μsec as would be expected for the reconstruction of hydrogen-containing structural units into Si_3B units.

The ^{31}P NMR chemical shifts in compensated a-Si:H indicated an increase in fourfold phosphorus over the uncompensated material and this increase has been interpreted in terms of a model involving the formation of boron-phosphorous complexes.¹² The experimental uncertainties of the ^{11}B linewidths and coupling constants do not allow us to distinguish between threefold structural units containing B-P or B-H bonds. We can, however, rule out the presence of significant numbers ($\sim 10\%$) of fourfold sites such as $\text{Si}_3\text{P-BSi}_3$. In most B-P complexes reported in the literature, both the boron and phosphorous are fourfold coordinated.¹⁶ Therefore absence of a detectable signal due to fourfold coordinated boron strongly suggests that there is not a significant concentration of such complexes in this film. It has been suggested that compensation would result in occupation of the boron p_z -orbital (corresponding to a change in hybridization from sp^2 to sp^3), leading to a significantly narrower NMR line.¹⁰ We find no evidence for such a mechanism, although there may be a small effect which is masked by the uncertainties in the linewidths. In addition, electron spin resonance experiments give no indication of a line due to such a state.

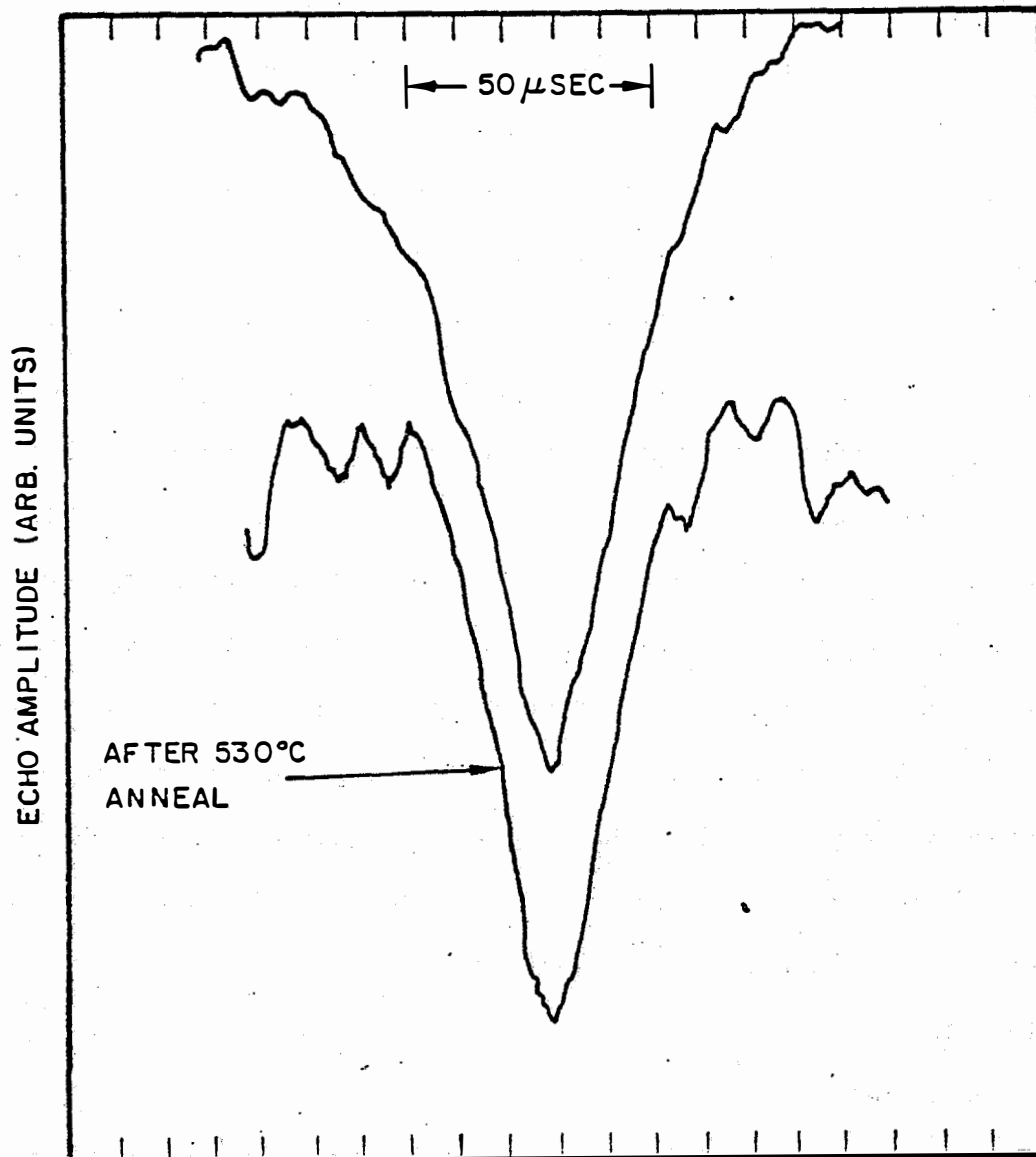


Fig. 2. The effect of annealing on the spin echo ($\nu_0=76$ MHz) of the 0.7 at Boron sample (IBM).

The inverse dipolar linewidth due to mutually resonant spins, T_2 , gives a rough measure of average spin-spin distance and, when compared to the concentration, of the degree of clustering of boron atoms within the film. For the IBM and BNL films we measure 850 μsec and 800 μsec respectively for T_2 . On the other hand for a random distribution of boron atoms at this concentration we would expect $T_2 \sim 9 \text{ msec}$. This clearly indicates that the boron in these films is clustered (The average B-B distance is $\sim 6 \text{ \AA}$). On the other hand, the expected dipolar contributions for small boron-boron separations such as occur in B-B bonds or B_2H_6 molecules predict much more rapid T_2 decays than are observed. In addition, experimental observations in solid boron and boron carbide yield values¹⁷ for T_2 which are an order of magnitude smaller than that which is observed in $\text{a-Si}:(\text{H},\text{B})$. Thus the NMR measurements suggest that few B-B bonds or B_2H_6 molecules exist in our films. These conclusions are consistent with those drawn from infrared measurements of Shen and Cardona.¹⁸

To summarize the results of our ^{11}B NMR experiments to date: (1) The boron is predominantly bonded the hydrogen containing units such as Si_2BH , (2) No evidence for B-P complexes has been observed, and (3) The boron is clustered in relatively boron rich regions.

B. ESR Results

1. Carbon Center

Although most of the ESR work in a-Si:H has focused on the trivalent silicon atom with a resonance at $g=2.0055$, a number of other centers have also been observed. Lines at $g=2.013$ and $g=2.004$ are observed in heavily boron doped and heavily phosphorous doped samples respectively. These are attributed to band tail states¹⁹ or possibly to twofold coordinated silicon atoms.²⁰ In addition, defects due to impurities such as nitrogen, oxygen and

transition metals have been observed. In $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films a strong resonance at $g=2.003$ is observed and has been attributed to dangling bonds on carbon atoms.²¹ Dersch and coworkers have reported a similar line at $g=2.0028$ ²² and speculated that it could be due to defects at internal surfaces but have reported no detailed work on this line. We have recently completed a more detailed study of this defect³ (Appendix C) and can conclude that this line is due to carbon within the film.

Three different samples were used in this work, the two which were also used in the NMR work and a third undoped film obtained from Brookhaven. No significant sample to sample variations were observed. Samples were annealed either under vacuum or in a helium atmosphere. Either annealing procedure increased the intensity of the carbon line in roughly the same manner, indicating that this not an artifact of the annealing procedure.

The spectra before annealing and after two different annealing temperatures are shown in Fig. 3. There are two lines present; one at $g=2.0055$ due to silicon dangling bonds and a second sharper line at $g=2.0026$ ($H=12.52$ kG) which is the focus of this work. It should be noted that the small shifts in the positions of the lines are due to changes in the resonant frequency of the cavity and not to changes in the g -values of the resonances. It is seen that the $g=2.0026$ line is present even before annealing but that its intensity is significantly increased by annealing.

In Fig. 4 the spectra at resonant frequencies of 35 GHz and 9.3 GHz are compared. As has been shown by Dersch and coworkers,²² the $g=2.0055$ line is inhomogeneously broadened due to a distribution in g -values and therefore its linewidth is proportional to frequency. The $g=2.0026$ line is however basically a homogeneously broadened line and hence its linewidth is nearly independent of resonant frequency.

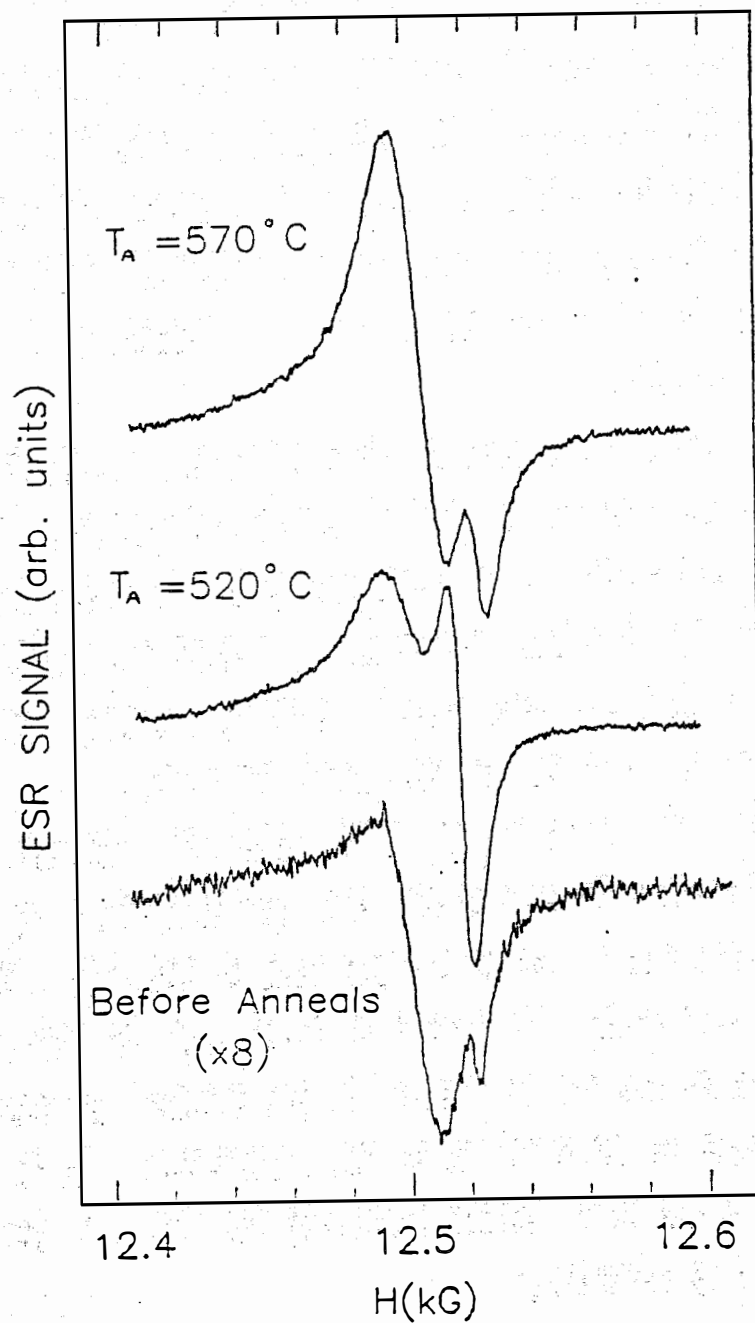


Fig. 3. The ESR spectra taken at 35 GHz of one of the Brookhaven samples before annealing and after the indicated annealing temperatures.

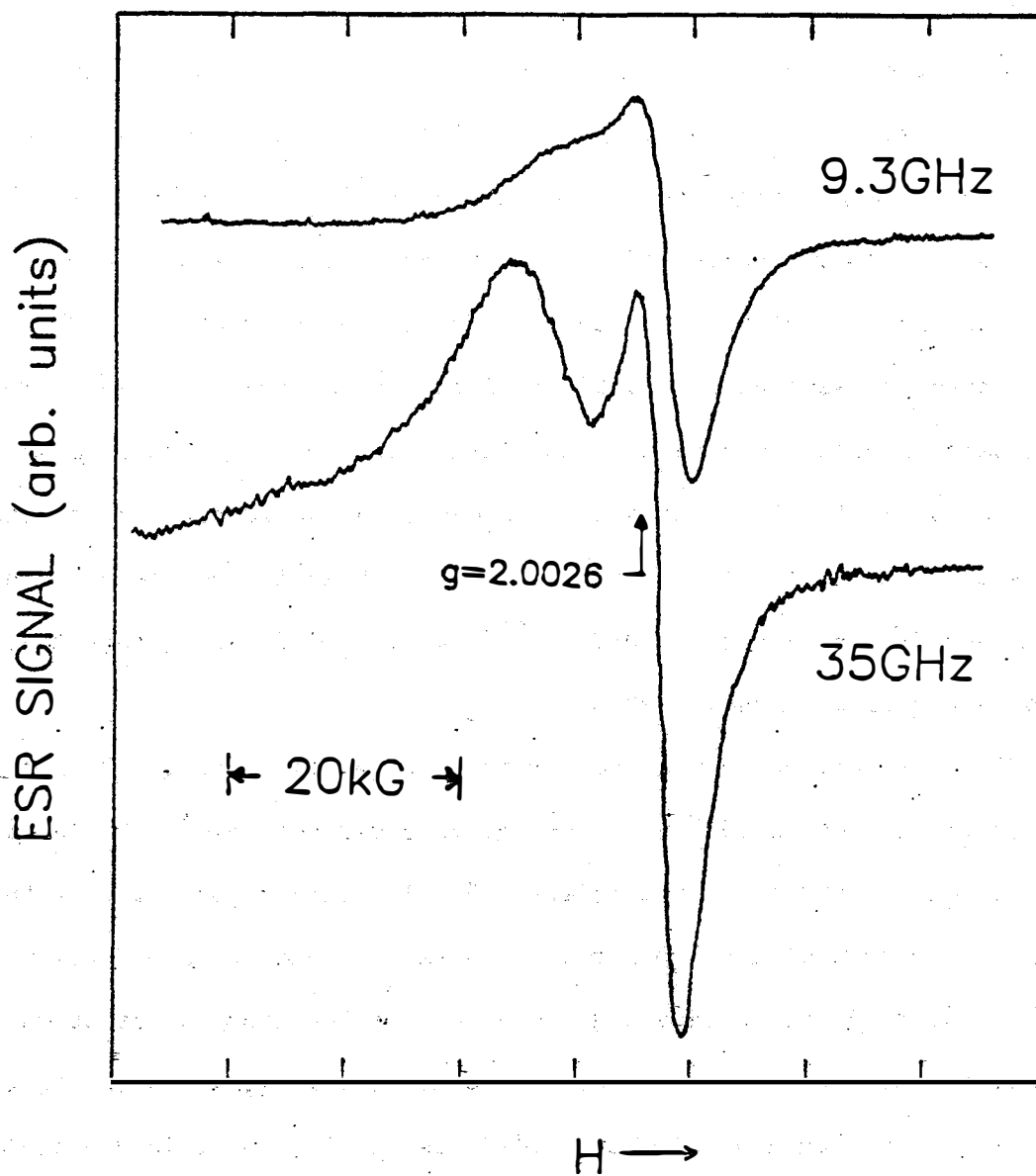


Fig. 4. The ESR spectra at 9.3 GHz and at 35 GHz of the IBM sample after annealing to 500°C. The spectra have been shifted so that the central portions are aligned.

As shown in Fig. 3, the intensity of this line is strongly affected by annealing temperature. This is shown in detail in Fig. 5 which gives the intensity of this line as a function of annealing temperature. Extension of the low temperature portion of the curve to room temperature gives a good fit with the results before annealing and yields an activation energy of about 0.2 eV. On the high temperature side, the curve is much steeper and while there are too few data to determine whether the process is activated, a straight line through the points gives an activation energy of about 1 eV.

There are several models to consider for the $g=2.0026$ line. Two possible intrinsic defects are a negatively charged divalent silicon atom and a dangling bond at an internal surface. However, one would not expect either defect to yield a homogeneously broadened line such as is seen here. Furthermore, this same defect is seen in a-Ge:H.²³ clearly indicating that this resonance line is due to an impurity atom.

The more obvious candidate for this center is carbon. Typical glow discharge films contain 10^{19} to 10^{20} carbon atoms per cc.²⁴ While the maximum signal seen by ESR is on the order of 5×10^{17} centers per cc. Furthermore, as mentioned previously, a similar line is seen in a-Si_xC_{1-x}:H alloys²¹ and has been associated with a dangling bond on a carbon atom. For atoms with small atomic number such as carbon the spin-orbit coupling, which shifts the g -value from the free electron value of 2.0023, is small, so it is difficult to distinguish one carbon center from another solely on the basis of the g -value.

Miller and Haneman²⁵ have seen a similar resonance on samples crushed in vacuum and argued that it was due to hydrocarbons adsorbed onto the surface. However, in their work the resonance was not detectable after exposure to air, while in the present study the signal is quite stable even after exposure to

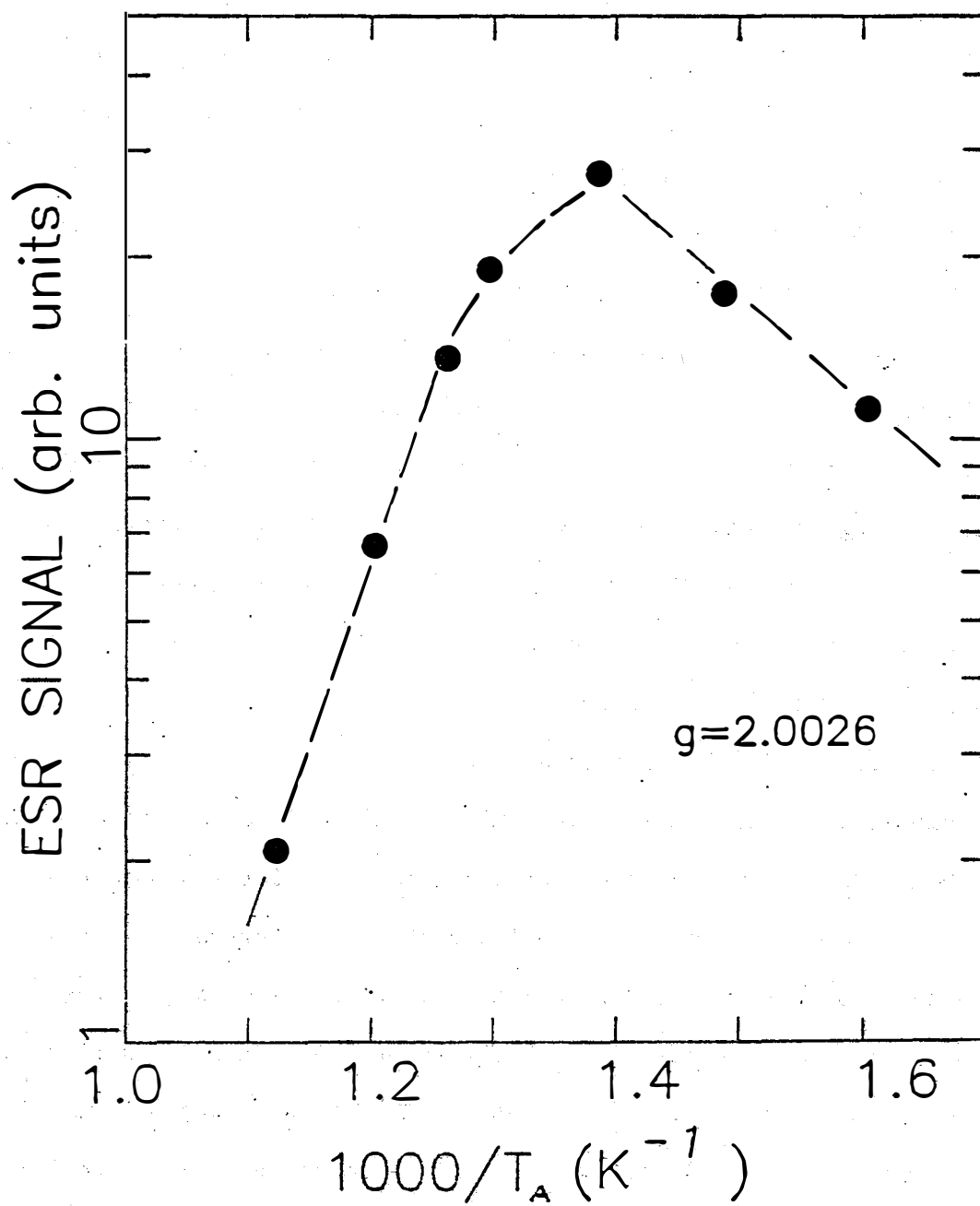


Fig. 5. The annealing behavior of the carbon line in the compensated sample.

air for several days. It therefore seems reasonable to conclude that the carbon has been incorporated into the bulk of the film during deposition. From the annealing data it seems likely that as the sample is heated C-H bonds are broken releasing hydrogen and creating paramagnetic centers. A similar activation energy is seen for hydrogen evolution from a-Si:H.⁶ The sharp drop in the number of centers would then be due to a reconstruction process taking place before the sample actually crystallizes at about 600°C.

We cannot, at present, say how the carbon impurities could affect the electronic properties of the amorphous silicon films. One might speculate that a simple dangling bond on a carbon atom might yield a state in the gap as the silicon dangling bond does. The resolution of this question could come from measurements on the UHV films grown by the Xerox group in which the impurity content is significantly reduced.

2. Measurements on CVD Films

We have performed ESR measurements on LPCVD a-Si:H provided by Chronar and the University of Delaware. The only signal seen is the $g=2.0055$ silicon dangling bond line. The spin densities and details of the sample preparation are given in Table 1. The spin densities are given per unit area since the defect density is somewhat larger near the growth surface than in the bulk of the film. This point is more clearly illustrated by the results of etch back experiments shown in Fig. 6. In this experiment we have progressively removed the silicon film from the substrate using a KOH solution. From the ESR spectra taken after each etch we are able to do a depth profile of the spin density as shown for three films in Fig. 6. This indicates that the spin density is about three times as high near the growth surface of the film as in the bulk of the film. No significant difference is seen near the interface of the film with SiO₂ substrate, however.

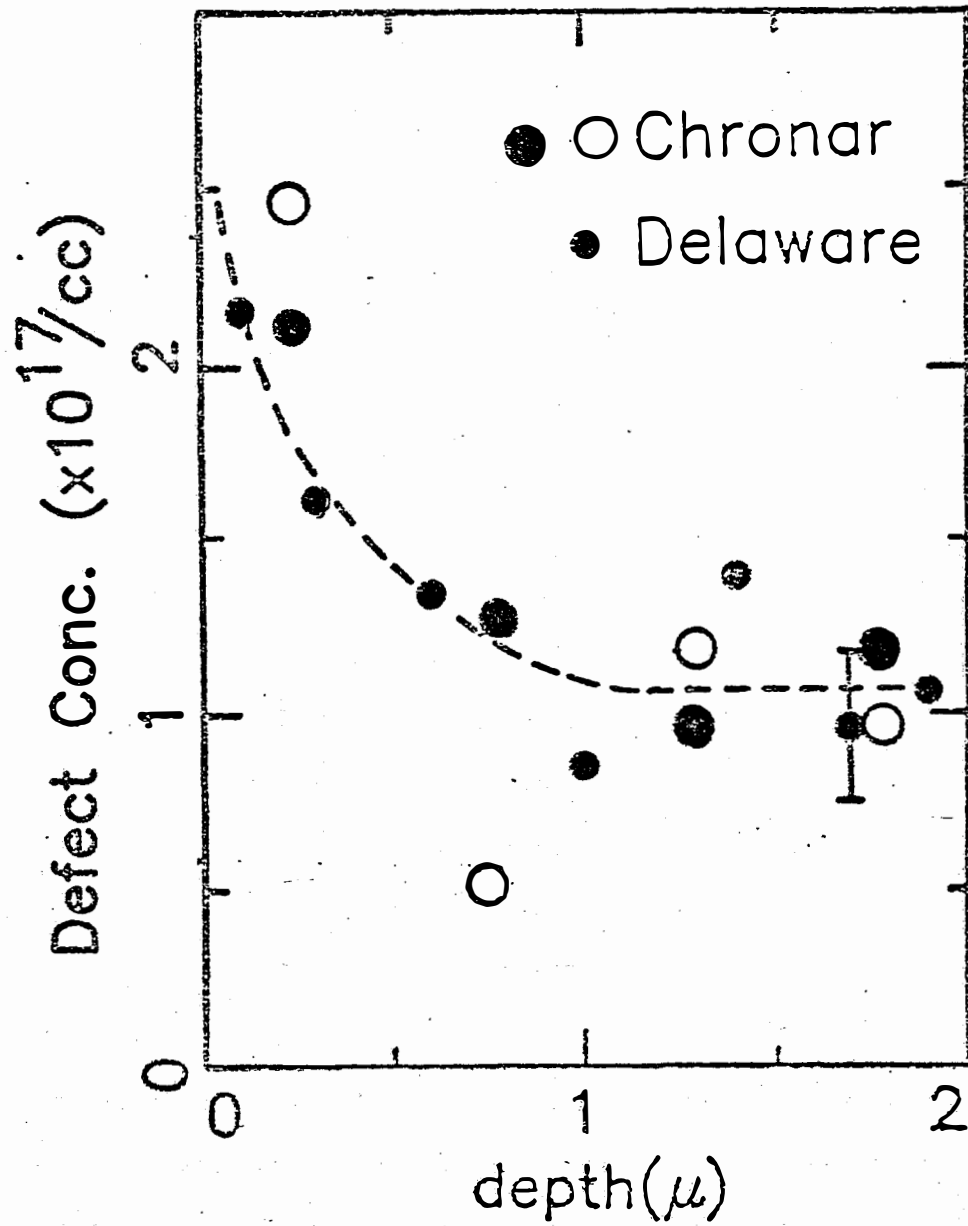


Fig. 6. The spin density in 3 LPCVD films as a function of distance from the growth surface.

If the increased defect density near the growth surface presents a significant problem in device manufacturing, it should be corrected easily by either a modification of the method by which the reaction is turned off or by a simple etching procedure such as was employed here.

Table 1. LPCVD Sample Details

Source	#	Substrate Temp.(°C)	Method	Thickness (microns)	Spins/cm. ² (x10 ¹³)
Del.	240-5	400	Flow	1	8
Del.	240-6	400	Flow	1.5	8
Del.	240-7	400	Flow	2	8
Del.	223-C	430	Flow	2	8
Del.	223-D	430	Flow	2	11
Chronar	735	470	Static	0.5	4
Chronar	736	470	Static	1	5
Chronar	737	470	Static	2	6
Chronar	745	470	Flow	1	5
Chronar	746	470	Flow	0.5	3
Chronar	747	470	Flow	2	9

Delaware 240 series were grown in 360 min. at 24 Torr. of disilane. The different thicknesses correspond to different positions in the tube. The 223 series was grown in 210 min. at 30 Torr. of disilane.

Chronar samples were grown at 20 Torr. of disilane at a rate of about .06 microns/min. The flow method material is some of the first which they grew and later runs have shown better electrical properties.

Task 1.2 Light Induced Effects

The Stabler-Wronski effect was first observed as a decrease in photoconductivity²⁷ after prolonged exposure to strong illumination. This effect is seen in ESR as an increase in the dangling bond line after exposure to light. Results for a glow discharge sample are shown in Fig. 7. The increase in the number of dangling bonds corresponds to an increase in trap density and hence, a decrease in carrier lifetime and photoconductivity.

The origins of this effect are still the subject of considerable controversy.²⁸⁻³¹ It was the initial opinion of our group and others that this could be due to impurities such as carbon or oxygen. However more recent results clearly indicate that this is not the case.³² It should be noted that this effect is not unique to a-Si:H and that quite stable and similar ESR centers may be induced in SiO₂ by sub-band gap light.³³ (Note that the band gap of SiO₂ is ~10eV.) and with higher energy photons.³⁴

In the case of SiO₂ there is significant variation in the sensitivity depending on processing steps and so one might expect that the sensitivity of a-Si:H would also vary with processing. Indeed there are indications that the photoconductivity of CVD prepared films is not strongly affected by light. The ESR spectrum in the films investigated was also not affected by prolonged exposure to strong light. However, it should be noted that these samples have ~10¹⁷ spins/cc while good glow discharge material has only ~10¹⁵ spins/cc. We could then induce ~10¹⁶ spins/cc in each and see a dramatic effect in the glow discharge material and only a slight effect in the CVD material. Clearly more work needs to be done on very high quality CVD films to determine the nature of this effect in those materials.

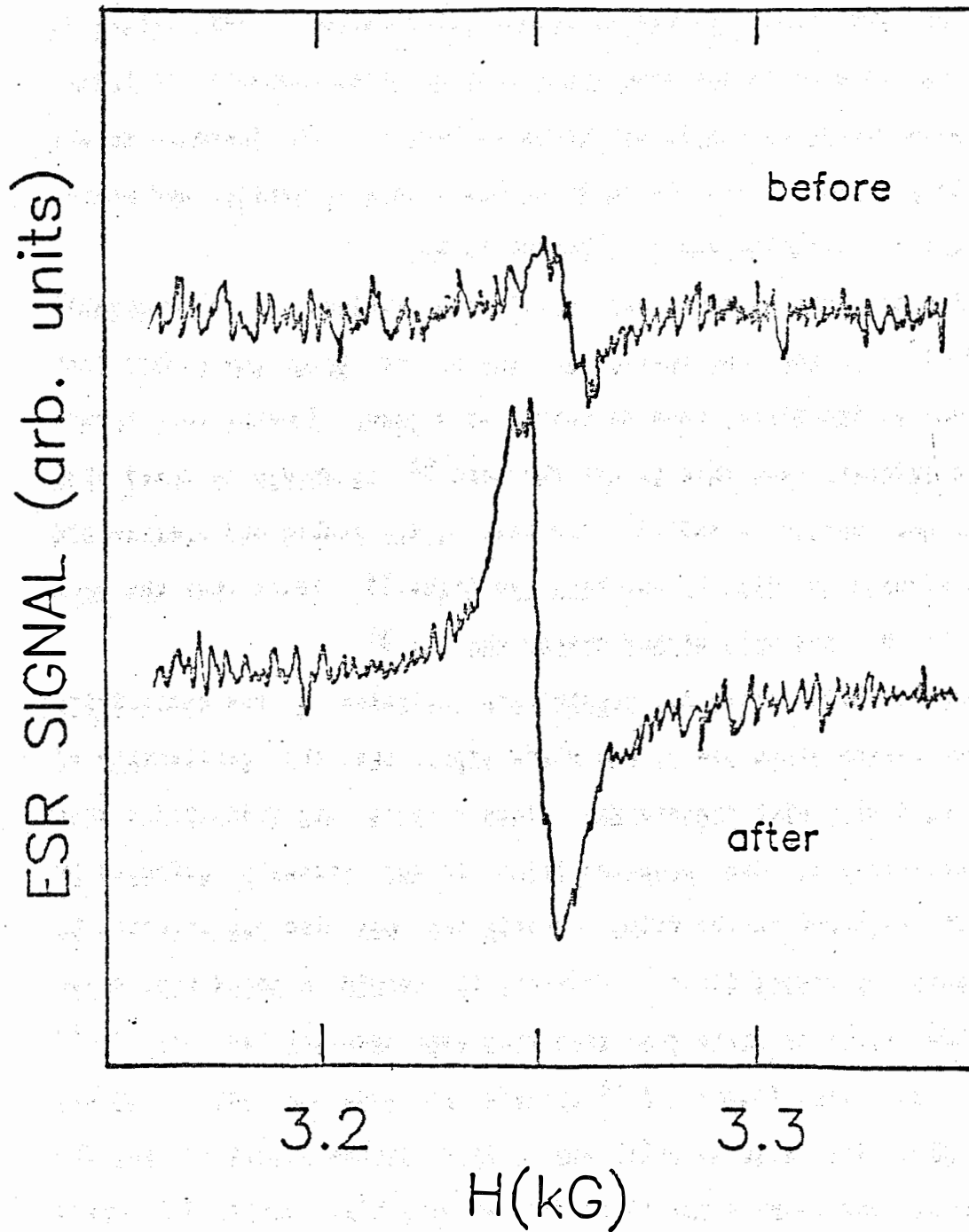


Fig. 7. The central ($g=2.0055$) ESR line before and after light soaking for an intrinsic glow discharge sample.

Task 1.3 Studies of Microcrystalline Films

Microcrystalline silicon ($\mu\text{-Si}$) is composed of very small ($\sim 100\text{\AA}$) crystals of silicon embedded in an matrix of a-Si:H . Crystalline silicon is much more transparent than amorphous silicon, so the microcrystalline film provides a "window" into the pn junction of a solar cell. This material must be doped with either boron or phosphorous.

It is the intention of this work to help understand where the dopants in these films are located. As mentioned previously, boron and phosphorous doped a-Si:H give distinct ESR lines at $g=2.013$ and $g=2.0043$ respectively. At low temperatures ($\leq 30\text{K}$) crystalline P-doped silicon has a sharp line at $g \approx 1.997$ due to conduction electrons at high doping levels and at lower doping levels a doublet split by 42G and centered about this g -value is observed.³⁵ Boron doped crystalline silicon³⁶ is more complicated and a resonance will appear only in a stressed sample. In principle a great deal of information about the location of the dopants should be obtainable from the ESR spectrum. We have looked at three films, one highly phosphorous doped and the other two highly boron doped. All were provided by Brookhaven National Laboratory. In the phosphorous doped film we see only the resonance due to the conduction electrons in the crystalline material and no resonance from the amorphous matrix. This clearly indicates that the phosphorous is incorporated into the crystals and is active as a dopant.

In the boron doped films we see no resonance at all and while this is disappointing it can be explained in only one way. The boron must also be incorporated into the crystals and furthermore the crystals must be under relatively low stress. If the crystals were stressed or if most of the boron were in the amorphous matrix then we would see a resonance.

While we still need to look at more films with a wider range of doping levels, it seems clear that ESR could prove to be an extremely informative probe of dopants in $\mu\text{-Si}$.

References

1. S.G. Greenbaum, W.E. Carlos and P.C. Taylor, *Physica* 117B & 118B, 886 (1983).
2. S.G. Greenbaum, W.E. Carlos and P.C. Taylor, *Journal of Applied Physics*, to be published.
3. W.E. Carlos, *Journal of Noncrystalline Solids*, to be published.
4. W.E. Spear, P.G. LeComber, *Sol. State Comm.* 17, 1193 (1975)
5. J.C. Knights, *Phil. Mag.* 34, 663 (1976).
6. J.A. Reimer, R.W. Vaughan, J.C. Knights, *Phys. Rev. B* 24, 3360 (1981).
7. D.E. Carlson, R.W. Smith, C.W. Magee, P.J. Zanzucchi, *Phil. Mag.* B45, 51 (1982).
8. A. Matsuda, M. Matsumura, K. Nakagawa, T. Imura, H. Yamamoto, S. Yamasaki, H. Okuski, S. Iizima, K. Tanaka, Proc. Topical Conf. Tetrahedrally Bonded Amorphous Semiconductor, Carefree, 1981, AIP Conf. Proc. No. 73, 192 (1981).
9. S. Yamasaki, A. Matsuda, K. Tanaka, *Japan J. Appl. Phys.* 21, L789 (1983).
10. J. Robertson, *Phys. Rev. B* 28, 4666 (1983).
11. J.C. Knights, T.M. Hynes, J.C. Mikkelsen, Jr., *Phys. Rev. Lett.* B 39, 712 (1977).
12. J.A. Reimer, T.M. Duncan, *Phys. Rev.* B27, 4895 (1983).
13. S.G. Greenbaum, W.E. Carlos, P.C. Taylor, *Sol. State Comm.* 43, 663 (1982).
14. G.C. Brown, D.F. Holcomb, *Phys. Rev. B* 10, 3394 (1974).
15. H.M. Kriz, P.J. Bray, *J. Magn. Reson.* 4, 76 (1971).
16. W.G. Henderson and E.F. Mooney in Annual Review of NMR Spectroscopy, Vol. 2, ed. E.F. Mooney (Academic Press, London, 1969), p. 219.

17. T.V. Hynes, M.N. Alexander, J. Chem. Phys. 54, 5296 (1971).
18. S.C. Shen, M. Cardona, Phys. Rev. B 23, 5322 (1981).
19. J.C. Knights, D.K. Biegelsen and I. Solomon, Solid State Commun. 22, 133 (1977)
20. D. Adler and F.R. Shapiro, Physica 117B & 118B, 932 (1983).
21. A. Morimoto, T. Muira, M. Kumeda and T. Shimizu, Jap. J. Appl. Phys. 20 (1981) L833 and Jap. J. Appl. Phys. 21, L119 (1982) and J. Watanabe, Y. Hata, A. Morimoto and T. Shimizu, Jap. J. Appl. Phys. 21, L613 (1982).
22. H. Dersch, J. Stuke and J. Beichler, Phys. Status Solid B105 265 (1981).
23. M. Stutzmann, private communication.
24. C.C. Tsai, J.C. Knights and M.J. Thompson, Journal of Noncrystalline Solids, to be published.
25. D.J. Miller and D. Hanemann, Surf. Sci. 24, 639 (1971).
26. C.C. Tsai, H. Fritzsche, M.H. Tanielian, P.J. Gaczi, P.D. Persons and M.A. Vesaghi in Amorphous and Liquid Semiconductors, ed. W.E. Spear (Univ. of Edinburgh, 1977) pp. 339-343.
27. D.L. Staebler and C.R. Wronski, Appl. Phys. Lett. 31, 292 (1977); D.L. Staebler and C.R. Wronski, J. Appl. Phys. 51, 3262 (1980).
28. R.S. Crandall, Phys. Rev. B 24, 7457 (1981).
29. D. Adler, J. de Phys 42, C4-3 (1981)
30. H. Dersch, J. Stuke and J. Berchler, Appl. Phys. Lett. 38, 456 (1981).
31. S. Guha, J. Yang, W.C. Zubaty, S.J. Hudgens and M. Hack, Appl. Phys. Lett. 42, 588 (1983).
32. M. Stutzmann, C.C. Tsai and W.B. Jackson, Bull Am Phys. Soc. 29, 508 (1984).
33. J.H. Stathis and M.A. Kastner, Bull. Am. Phys. Soc. 29, 339 (1984).

34. For a review see D.L. Griscom, Journal of Non-Crystalline Solids 31, 241 (1978).
35. G. Feher, Phys. Rev. 114, 1219 (1959).
36. G. Feher, J.C. Hensel and E.A. Gere, Phys. Rev. Lett. 5, 309 (1960).

BORON AND HYDROGEN BONDING IN B-DOPED a-Si:H - AN NMR STUDY

S. G. Greenbaum, W. E. Carlos and P. C. Taylor

Naval Research Laboratory
Washington, D. C. 20375 USA

^{11}B and ^1H NMR measurements performed on boron-doped films of a-Si:H prepared by glow discharge are reported. A sample containing 10 atomic % B exhibits two distinct boron sites, both of them being threefold coordinated. A second sample containing 0.7 atomic % B shows only one boron site, also threefold coordinated. Measurements of the ^{11}B spin-spin relaxation time T_2 indicate that the boron sites are clustered in both the 10% B and 0.7% B materials. The temperature dependence of the ^1H spin-lattice relaxation time T_1 in the 10% B film does not exhibit the sharp T_1 minimum commonly observed in undoped a-Si:H films prepared by glow discharge. Suppression of the T_1 minimum in the B-containing material is explained in terms of a spin diffusion bottleneck in the relaxation pathway of the Si- or B-bonded protons in the film.

1. INTRODUCTION

Boron is routinely employed as a p-type dopant in films of hydrogenated amorphous silicon (a-Si:H). Although it is known that only a small fraction of the boron atoms ($<0.1\%$) is effective in doping, the local bonding configurations of the vast majority of the boron atoms are not well known. For this reason, ^{11}B and ^1H NMR measurements have been performed on films of B-doped a-Si:H prepared by the glow discharge technique.

This paper represents an extension of a previously reported ^{11}B NMR study of a B-doped a-Si:H film.¹ Those results will be summarized here, and new ^1H NMR spin-lattice relaxation (T_1) measurements performed on the same sample will be presented and discussed. In addition, preliminary ^{11}B data taken on a second B-doped a-Si:H film will be discussed. The sample obtained from RCA (hereafter denoted as "RCA") was a $\sim 3\ \mu\text{m}$ film prepared on an aluminum substrate heated to 230C, and contained $\sim 10\ \text{at.}\%$ of both B and H. The other sample (denoted as "IBM") was prepared at IBM in a similar manner, differing only in substrate temperature (275C) and B concentration ($\sim 0.7\ \text{at.}\%$ B). Experimental details concerning the NMR measurements can be found elsewhere.^{1,2}

2. RESULTS AND DISCUSSION

Figure 1 (taken from ref. 1) shows the Fourier transformed ^{11}B NMR spin-echo signal at 61 MHz for RCA. There are clearly two components to the lineshape, the broader line appearing as shoulders on the narrow line. The primary source of broadening for both lines is the ^{11}B nuclear quadrupole interaction, since the value found for the spin-spin relaxation time ($T_2 \sim 350\ \mu\text{sec}$) yields a dipolar linewidth of less than 1 KHz. Estimates of the quadrupole coupling constants (QCC) associated with each of the lines can be obtained following the procedure

described in ref. 1. It turns out that $\text{QCC} = 5.8 \pm 1.0\ \text{MHz}$ for the broad line and $\text{QCC} = 3.5 \pm 1.0\ \text{MHz}$ for the narrow line in Fig. 1. These QCC values are characteristic of boron atoms in threefold coordination, as four-coordinated borons almost always have $\text{QCC} \leq 1\ \text{MHz}$.³ Considerations based on a Townes-Dailey analysis^{1,4} suggest that the structural groupings that give rise to the lineshape in Fig. 1 are Si_2B units for the broad component and Si_2BH units for the narrow component. The 350 μsec T_2 value obtained for the RCA sample is nearly a factor of four smaller than that obtained for amorphous $3\text{B}_2\text{S}_3 \cdot 7\text{As}_2\text{S}_3$ (containing 12 at.% B). This provides convincing evidence that the boron structural units are clustered rather than randomly distributed in the RCA material.

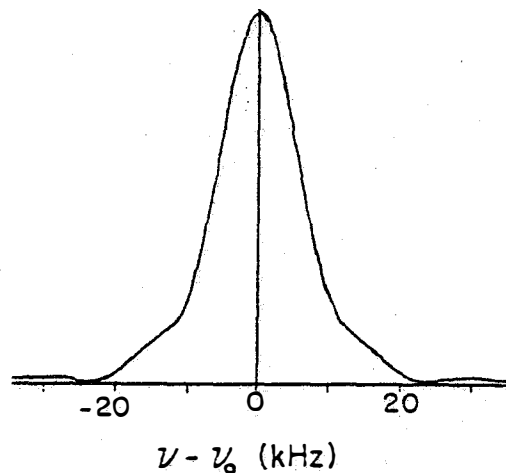


Figure 1: Fourier transformed ^{11}B NMR spin-echo signal at 61 MHz for RCA (from ref. 1).

Preliminary data for the IBM sample⁵ yield an NMR lineshape consistent with the presence of only one identifiable site which corresponds to the narrow component (attributed to Si₂BH units) of the RCA lineshape. The T₂ value found for IBM is 850±20 μsec which indicates substantial clustering of the boron units since one would expect roughly a tenfold increase in T₂ over RCA, simply based on the relative boron concentrations in the two sample.

Previous proton NMR studies of undoped a-Si:H^{6,7} have revealed the presence of two distinct hydrogen environments, isolated from each other. Although preparation conditions (e.g. deposition parameters, substrates, etc.) of the samples vary considerably, roughly the same proton NMR "signature" exists in all samples--a narrow (full width at half maximum FWHM ~4 kHz) Lorentzian line superimposed on a broad (FWHM ~25kHz) Gaussian line.² The proton lineshape in the boron-doped RCA film is well within the range of the undoped sample-to-sample lineshape variations, and therefore does not provide information regarding the existence of structural units containing boron-hydrogen bonds.

The temperature dependence of the proton spin-lattice relaxation time, T₁, has been studied for a wide variety of undoped a-Si:H films.^{2,7} All films prepared by glow discharge exhibit a relatively frequency independent T₁ minimum at about 30K. The T₁ behavior in undoped a-Si:H has been explained in terms of a model, originally proposed by Conradi and Norberg,⁸ in which trapped molecular hydrogen molecules act as the relaxation centers. Additional experiments performed in this laboratory² and by Reimer et al.⁹ support the basic picture of a small number of H₂ relaxation centers with the bulk of hydrogen (bonded to Si) being relaxed via a spin diffusion process.

It is reasoned that relaxation of the H₂ molecules (about 1% of the total hydrogen content of the films) accounts for the important features of the T₁ vs. temperature curve, in particular, the T₁ minimum. For the bonded hydrogen the spin-lattice relaxation time is given as²

$$T_1(H) = 3/8 T_1(H_2) [n(H)/n(O-H_2)] + T_1(SD) \quad (1)$$

where n(H) is the total concentration of hydrogen in the sample and n(O-H₂) is the concentration of orthohydrogen in the material. T₁(H₂) is the spin-lattice relaxation time for the orthohydrogen molecules, and T₁(SD) is a spin diffusion limited term which can produce a spin diffusion "bottleneck."

A simple test of this model is to examine the effect of conversion of the orthohydrogen (I=1) to parahydrogen (I=0) on T₁, since parahydrogen does not act as a relaxation center.² This conversion is a slow bimolecular process driven by the interaction between protons on adjacent H₂ molecules.¹⁰ The ortho-to-para ratio (OPR) can be substantially decreased simply by keeping

the sample at liquid helium temperature for several weeks (this ratio will be frozen in during the normal running of an experiment). The dependence of T₁ on temperature for RCA is displayed in Fig. 2.¹ The three "B-doped" curves correspond to different OPR's obtained by maintaining the sample at 4.2K for different lengths of time (0, 17, and 49 days). The T₁ behavior of a representative undoped film² is shown for comparison.

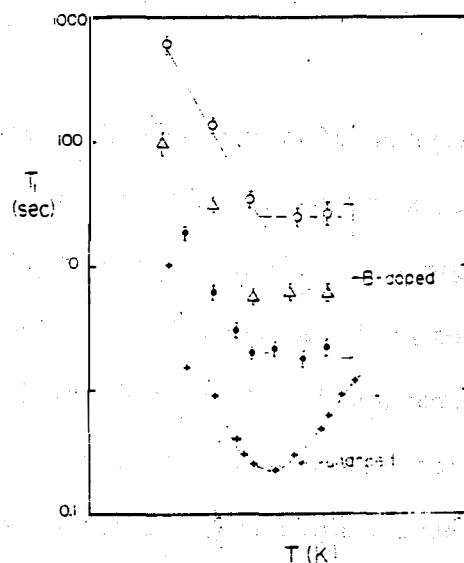


Figure 2: Temperature dependence of ¹H spin-lattice relaxation time T₁ for: (a) crosses-undoped a-Si:H (from ref. 2); (b) filled circles-RCA; (c) triangles-RCA after 17 days held at 4.2K; (d) open circles-RCA after 49 days held at 4.2K. The curves drawn through the points are intended as aids in viewing the data.

It is clear that the shape of the T₁ vs. T curve is essentially unaffected by decreasing the OPR, although the magnitude of T₁ (at a given temperature) increases dramatically. This argues against the presence of significant relaxation processes (e.g. due to sample paramagnetism) that are independent of the OPR. It should be noted that annealing the sample at room temperature restored the values of T₁ initially measured (corresponding to the "0-days" curve). The most striking feature of the RCA T₁ vs. T curves is the lack of a well-defined T₁ minimum such as that observed in all undoped glow-discharge films studied to date.² Although T₁ does appear to attain its minimum value at ~30K, it remains at roughly the same value up to ~80K

Local Bonding Arrangements of Boron in Doped a-Si:H

S. G. Greenbaum^{*†} and W. E. Carlos
U.S. Naval Research Laboratory, Washington, D.C. 20375 USA

P. C. Taylor
Department of Physics, University of Utah, Salt Lake City, UT 84112 USA

Analysis of boron-11 NMR linewidths in films of boron-doped a-Si:H yields structural information concerning coordination and nearest neighbor bonding of the dopant atoms. A heavily doped (10 at.%B) film exhibits two distinct boron sites, both of them being threefold coordinated. A second sample containing 0.7 at.%B shows only one boron site, also threefold coordinated. Annealing studies of the latter sample suggest the formation of B-Si bonds as the hydrogen is driven off. The ^{11}B linewidth of a compensated film (containing 0.7 at.%B and 0.6 at.%P) is comparable to that of the uncompensated sample. ^{11}B spin-spin relaxation (T_2) measurements indicate that the boron sites are clustered in all three materials.

*National Research Council Postdoctoral Associate

†Present Address: Dept. of Physics and Astronomy, Hunter College (CUNY),
New York, New York 10021 USA

Introduction

Most device applications of amorphous tetrahedrally-bonded semiconductors depend on the controlled substitutional incorporation of Group III and Group V impurities. The high concentration of dopants required to achieve the desired doping levels in a-Si:H (as compared to c-Si) leads to the possible existence of midgap defect states associated with the nonsubstitutional impurities.^{1,2} Other undesirable phenomena possibly linked with doping include changes in morphology and hydrogen distribution,^{3,4} and gap-narrowing attributable to a decrease in the bonded H content of the a-Si:H network.⁵ Recent optical absorption measurements of heavily B-doped (~1 at.%) a-Si:H revealed an anomalously high absorption coefficient which was related to changes in texture and even mechanical stability of the films.⁶ In addition, cluster calculations of threefold-coordinated B in a-Si:H yielded energies that produce states in the gap while other trivalent Group-III elements were shown to be electronically passive.⁷

Knowledge of the local chemical environment of the dopant atoms in a-Si:H should provide a framework for the discussion of the electronic and optical properties attributable to the presence of large amounts of boron at non-substitutional sites. EXAFS studies of 1% As-doped a-Si:H showed that only $20 \pm 10\%$ of the As atoms were fourfold-coordinated,⁸ and ³¹P NMR chemical shift measurements yielded a ratio of threefold to fourfold P sites of roughly 4 to 1 in samples containing similar concentrations of P.⁹ Previously reported ¹¹B NMR quadrupole-broadened linewidths in heavily B-doped (10 at.%) a-Si:H were consistent with threefold coordination of at least 90% of the ¹¹B nuclei.¹⁰ In the present paper ¹¹B NMR are presented data for additional B-doped a-Si:H films, including a compensated sample. Results are compared with previously published measurements on heavily B-doped a-Si:H¹⁰.

Experimental Procedure

The a-Si:(H,B) films, obtained from different sources, were all prepared on Al substrates by glow discharge, and contained similar amounts of H (~10 at.%). A 3 μm , 25 mg sample containing 10 at.% B was obtained from RCA Laboratories. A second sample (IBM) from IBM Watson Research Center consisted of a 10 μm film (~600 mg) with 0.7% B. The compensated film, containing 0.7% B and 0.6% P and 7 μm thick (~500 mg), was provided by Brookhaven National Laboratory (BNL).

All NMR measurements were performed at room temperature with a Matec gated amplifier in conjunction with an Intermagnetics General superconducting solenoid and Nicolet model 1170 signal averager. The NMR frequency was varied from 45 to 150 MHz. Spin-lattice relaxation times (T_1) were determined by a repetition-rate technique, spin-spin relaxation times (T_2) were obtained from the spin-echo intensity dependence on pulse separation following a 90° - τ - 180° pulse sequence, and the inverse linewidth parameters (T_2^*) were extracted from either the free-induction-decay or the spin-echo. The relaxation processes were exponential within experimental error.

Results and Discussion

I. Linewidths

Figure 1a displays the spin-echo signal observed in the RCA sample at 61 MHz. It is clear that there are two components to the echo, each characterized by a separate T_2^* , ~13 μsec for the decay which transforms into a broad line in frequency space and ~20 μsec for the components which transforms into a narrower line. The spin-echo for the IBM samples at 1 MHz is shown in Fig. 1b, and appears to reflect a single component lineshape of approximately the same width as the narrow (in frequency space) line in the RCA sample. A similar line is seen for the BNL sample. The undistorted NMR absorption

spectra are, in principle, obtainable from either the free induction decay or echo signals by standard Fourier transform techniques. However, unless quadrature phase detection is employed (on resonance), possible asymmetries about the NMR frequency in the absorption spectrum will not be captured in the echo shape. Nevertheless one can still derive useful structural information from the echo decay constant T_2^* . The linewidth of a second-order quadrupole-broadened powder pattern corresponding to the central nuclear transition ($m=+\frac{1}{2} \rightarrow -\frac{1}{2}$) is proportional to $[e^2qQ]^2/h\nu_0$ when other sources of broadening can be neglected. In this expression e^2qQ/h is the nuclear quadrupole coupling constant, eq is the maximum component of the diagonalized electric field gradient tensor at the nuclear site, eQ is the ^{11}B quadrupole moment, and ν_0 is the NMR spectrometer frequency.¹¹ The electric field gradient is assumed to be axially symmetric. Figure 2 illustrates the dependence of the inverse linewidth parameter T_2^* on NMR frequency for both components of the echo in the RCA sample. The lines drawn through the points indicate that the absorption linewidths are inversely proportional to ν_0 as expected for the second-order quadrupole interaction. It is now possible to obtain an estimate of the quadrupole coupling constants associated with the separate lineshape components of the RCA sample simply by scaling their T_2^* 's to that measured for $3\text{B}_2\text{S}_3 \cdot 7\text{As}_2\text{S}_3$, for which $e^2qQ \sim 2.7/h$ MHz (also assumed axially symmetric).¹⁰ Similar dependences of the T_2^* 's of the IBM and BNL samples on ν_0 are observed and thus allow evaluation of their coupling constants in the same manner. The ^{11}B e^2qQ/h values are listed in Table I.

The magnitude of the quadrupole interaction observed in a-Si(H,B) provides convincing evidence that the ^{11}B nuclei ($\sim 90\%$ of the ^{11}B in the samples) giving rise to the observed linewidths are not tetrahedrally coordinated. For example, the ^{11}B linewidth in crystalline Si:B is $< 2 \text{ kHz}$ ¹² in accord with the

tetrahedral symmetry of the acceptor atoms; and, in borate minerals the ^{11}B quadrupole coupling constant is always found to be <0.9 MHz when the boron is four-coordinated and >2.4 MHz when it is three-coordinated regardless of the asymmetry of the nearest neighbor bonding.¹³

The boron sites in RCA have been tentatively identified as a boron atom bonded to three silicon atoms (BSi_3) corresponding to the broad line ($e^2qQ/h=5.8$ MHz) and a boron atom bonded to two silicon atoms and a hydrogen atom (Si_2BH) or possibly bonded to two hydrogen atoms and one silicon atom (SiBH_2) for the narrow line ($e^2qQ/h=3.5$ MHz).¹⁰ We conclude that the linewidths of the IBM and the BNL samples are consistent with the presence of Si_2BH or SiBH_2 units in both materials. ^{31}P NMR chemical shifts in compensated a-Si:H indicate an increase in fourfold phosphorus and this increase has been interpreted in terms of a model involving the formation of boron-phosphorus complexes.⁹ The experimental uncertainties of the ^{11}B linewidths and coupling constants do not allow us to distinguish between threefold structural units containing B-P or B-H bonds. We can, however, rule out the presence of significant numbers ($\sim 10\%$) of fourfold sites such as $\text{Si}_3\text{P}-\text{BSi}_3$. In most B-P complexes reported in the literature, both the boron and phosphorus are fourfold coordinated.¹⁴ Therefore absence of a detectable signal due to fourfold coordinated boron strongly suggests that there is not a significant concentration of such complexes in this film. It has been suggested that compensation would result in occupation of the boron p_z -orbital (corresponding to a change in hybridization from sp^2 to sp^3), leading to a significantly narrower NMR line.⁷ We find no evidence for such a mechanism, although there may be a small effect which is masked by the uncertainties in the linewidths. In addition, electron spin resonance experiments give no indication of a line due to such a state.

The IBM sample was annealed at 550°C resulting in the removal of ~75% of the hydrogen. The resulting linewidth was observed to broaden to approximately that of the broad component of the RCA sample. This result lends further support to the original site assignments. Figure 3 shows the unannealed and annealed IBM ^{11}B spin-echoes.

II. Relaxation Times

The room temperature ^{11}B T_1 values for the three samples are listed in Table I, and are longer than those typically found in network glasses such as B_2O_3 .¹⁵ Thus, nuclear dipole coupling to paramagnetic centers does not appear to be the dominant relaxation mechanism. Spin-lattice relaxation of quadrupolar nuclei in amorphous materials proceeds primarily through the coupling of the nuclear quadrupole moment to the excitation spectrum associated with two-level-system (TLS) disorder modes.¹⁵ The long T_1 's of a-Si:(H,B) may be related to a lower density of TLS modes in comparison with materials such as a- B_2O_3 ; although the results of other techniques give differing results for the density of TLS modes in a-Si:H.¹⁶ However, the temperature and frequency dependences of ^{11}B T_1 in a-Si:(H,B) would have to be determined in order to demonstrate this point conclusively.

The ^{11}B T_2 's are also listed in Table I. T_2 represents the inverse dipolar linewidth due to mutually resonant spins. Contributions to the echo decay from heteronuclei such as ^1H can be neglected on the basis of ^{11}B NMR results for materials with higher concentrations of hydrogen.¹⁷ Experimental results for the standard sample $3\text{B}_2\text{S}_3 \cdot 7\text{As}_2\text{S}_3$, once again can be productively employed. In the boron-arsenic-sulfide glass it is reasonable to assume that the boron is randomly distributed on what would otherwise be arsenic sites in pure As_2S_3 . The T_2 of 1300 μsec in $3\text{B}_2\text{S}_3 \cdot 7\text{As}_2\text{S}_3$ ¹⁰ provides clear evidence that the more rapid T_2 in the RCA sample (containing a similar concentration

of B) results from significant clustering of the boron structural units in the film. Similar conclusions can be drawn for the IBM and the BNL samples since their T_2 values are also too small to result from a random distribution of 0.7 at.% boron. It should be noted that, to within experimental resolution, the two separate components in the RCA sample have the same T_2 .

The T_2 results also place limits on the degree of boron clustering in a-Si:(H,B). Calculations of the expected dipolar contributions for small boron-boron separations such as occur in B-B bonds or B_2H_6 molecules predict much more rapid T_2 decays than are observed. In addition, experimental observations in solid boron and boron carbide yield values¹⁸ for T_2 which are an order of magnitude smaller than that which is observed in a-Si:(H,B). Thus the NMR measurements suggest that few B-B bonds or B_2H_6 molecules exist in our films. These conclusions are consistent with those drawn from infrared measurements of Shen and Cardona.¹⁹

Acknowledgements

The authors gratefully acknowledge J. A. Reimer (IBM), D. E. Carlson (RCA), and P.E. Vanier (BNL) for supplying the samples employed in this investigation. This work was supported in part by DoE Contract DE-AI02-80-C-83116 administered by SERI.

References

1. W. E. Spear, P. G. LeComber, Sol. State Comm. 17, 1193 (1975).
2. J. C. Knights, Phil. Mag. 34, 663 (1976).
3. J. A. Reimer, R. W. Vaughan, J. C. Knights, Phys. Rev. B24, 3360 (1981).
4. D. E. Carlson, R. W. Smith, C. W. Magee, P. J. Zanzucchi, Phil. Mag. B45, 51 (1982).
5. A. Matsuda, M. Matsumura, K. Nakagawa, T. Imura, H. Yamamoto, S. Yamasaki, H. Okushi, S. Iizima, K. Tanaka, Proc. Topical Conf. Tetrahedrally Bonded Amorphous Semiconductors, Carefree, 1981, AIP Conf. Proc. No. 73, 192 (1981).
6. S. Yamasaki, A. Matsuda, K. Tanaka, Japan J. Appl. Phys. L789 (1983).
7. J. Robertson, Phys. Rev. B 28, 4666 (1983).
8. J. C. Knights, T. M. Hayes, J. C. Mikkelsen, Jr., Phys. Rev. Lett. 39, 712 (1977).
9. J. A. Reimer, T. M. Duncan, Phys. Rev. B27, 4895 (1983).
10. S. G. Greenbaum, W. E. Carlos, P. C. Taylor, Sol. State Comm. 43, 663 (1982).
11. M. H. Cohen, F. Reif, in Solid State Physics 5, ed. F. Seitz and D. Turnbull (Academic Press, New York, 1957).
12. G. C. Brown, D. F. Holcomb, Phys. Rev. B10, 3394 (1974).
13. H. M. Kriz, P. J. Bray, J. Magn. Reson. 4, 76 (1971).
14. J. Szeftel, H. Alloul, J. Non-Cryst. Solids 29, 253 (1978).
15. W/ G/ Jemderspm amd E. F. Mooney in Annual Review of NMR Spectroscopy, Vol. 2, ed. E.F. Mooney (Academic Press, London, 1969), p. 219.
16. M. von Haumer, U. Strom, and S. Hunklinger, Phys. Rev. Lett. 44, 84 (1980); J.E. Graebmer, B. Golding, L.C. Allen, J.C. Knights, and J.K. Biegelsen, to be published.

17. R. T. Paine, E. Fukushima, S. B. W. Roeder, Chem. Phys. Lett. 32, 566 (1975).
18. T. V. Hynes, M. N. Alexander, J. Chem. Phys. 54, 5296 (1971).
18. S. C. Shen, M. Cardona, Phys. Rev. B23, 5322 (1981).

Table I

Sample (source)	at.%B	^{11}B inverse linewidth $T_2^*(\mu\text{sec})$ at $\nu_0 = 61 \text{ MHz}$		^{11}B $e^2qQ/h(\text{MHz})$		$T_2(\mu\text{sec})$	$T_1(\text{sec})$
RCA	10	12	(broad)	5.8	(broad)	350*	8.5*
		20	(narrow)	3.5	(narrow)		
IBM	0.7	23		4.0		850	~15
BNL	0.7**	23		4.0		800	~15

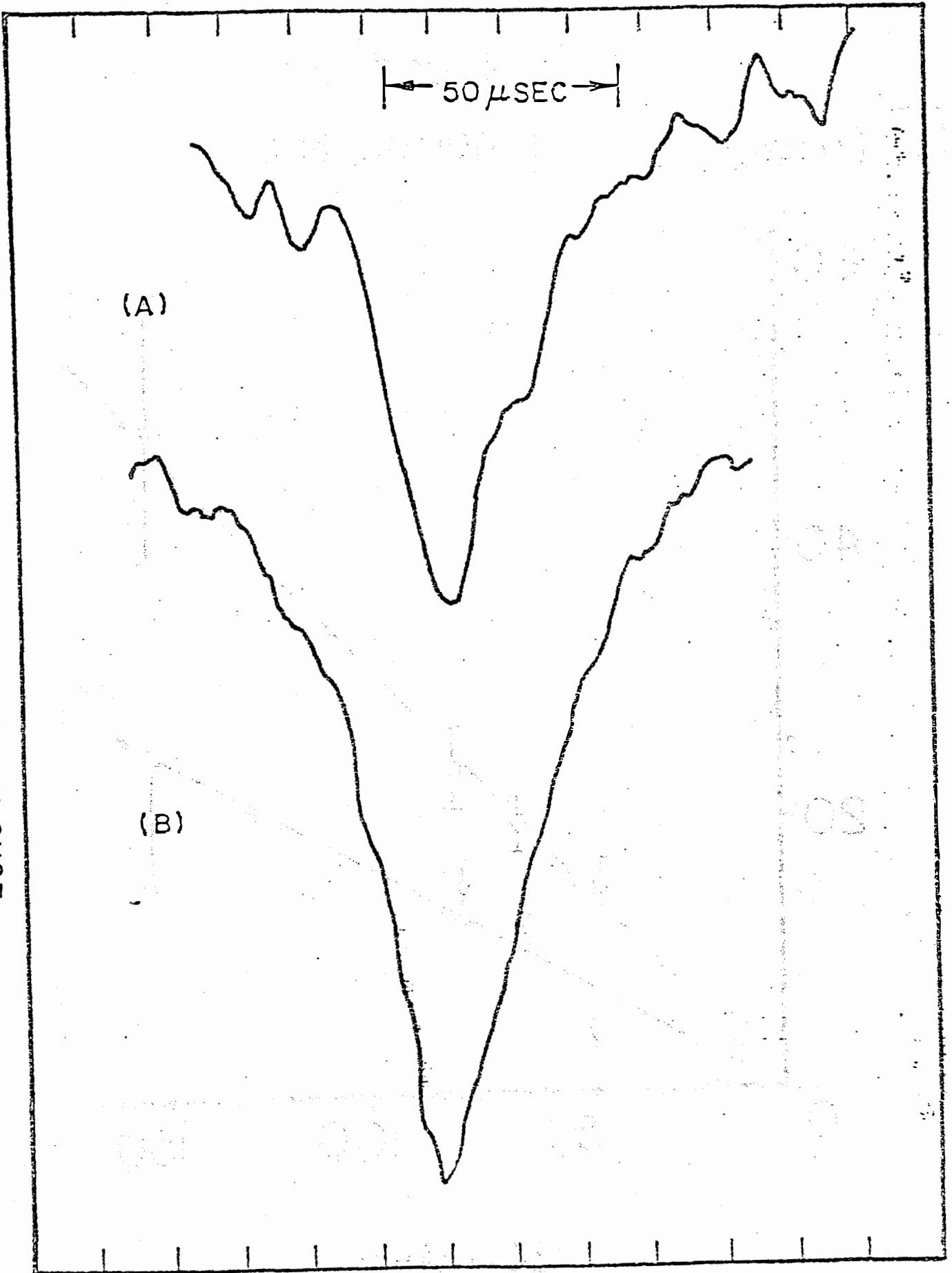
* average value for both broad and narrow components

** also contains 0.6% P

Figure Captions

- Fig. 1. Spin-echo signal to a) RCA at $\nu_0 = 61$ MHz; b) IBM at $\nu_0 = 60$ MHz
- Fig. 2. Inverse linewidth parameter T_2^* versus NMR frequency for separate lineshape components. Straight lines are drawn simply as an aid in viewing the data points.
- Fig. 3. The effect of annealing on the spin echo ($\nu_0 = 76$ MHz) of the 0.7 at.% Boron sample (IBM).

ECHO AMPLITUDE (ARB. UNITS)



T_2^* (μsec)

▽ broad line

○ narrow line

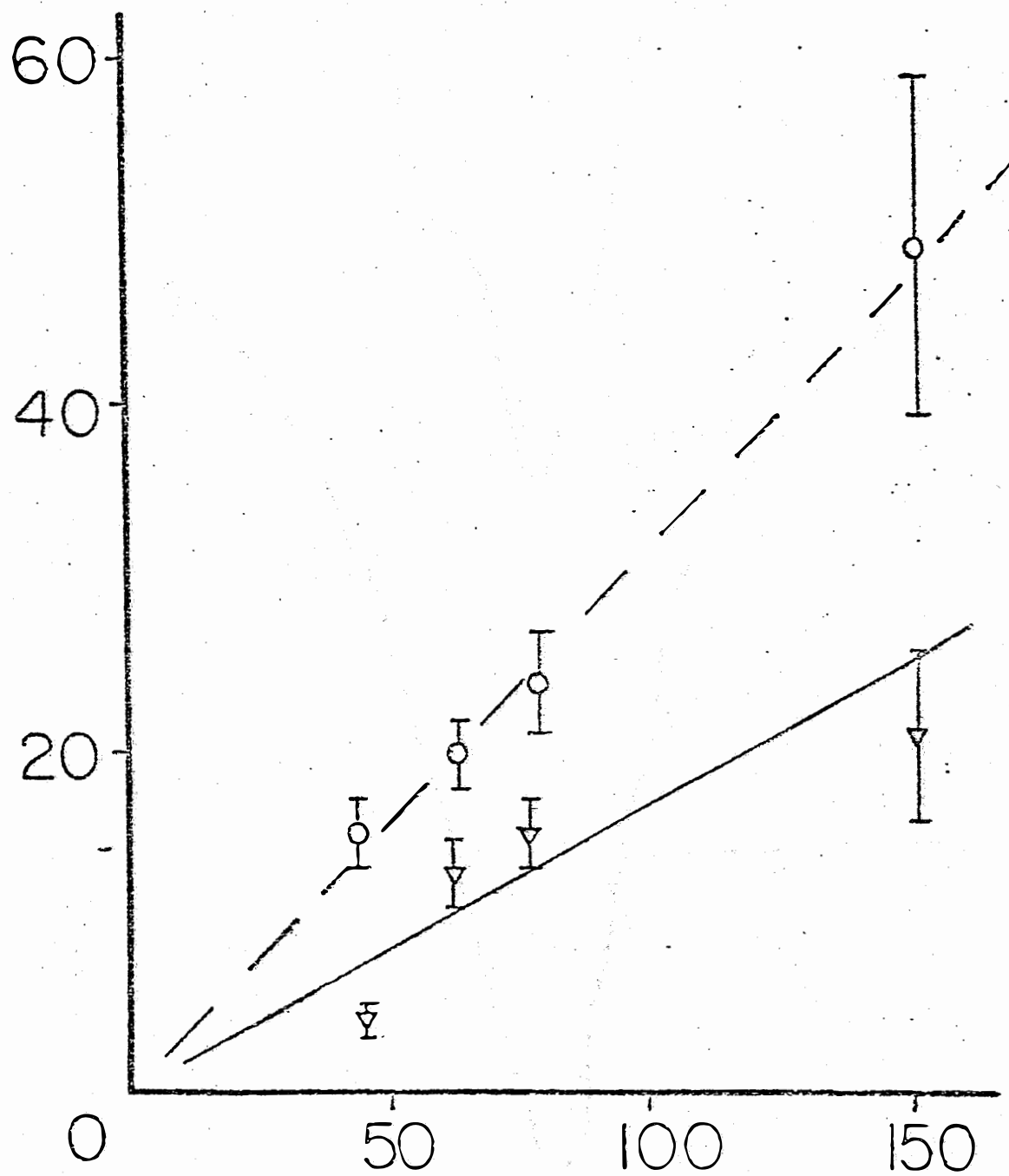


Fig 2

ν_0 (MHz)

ECHO AMPLITUDE (ARB. UNITS)

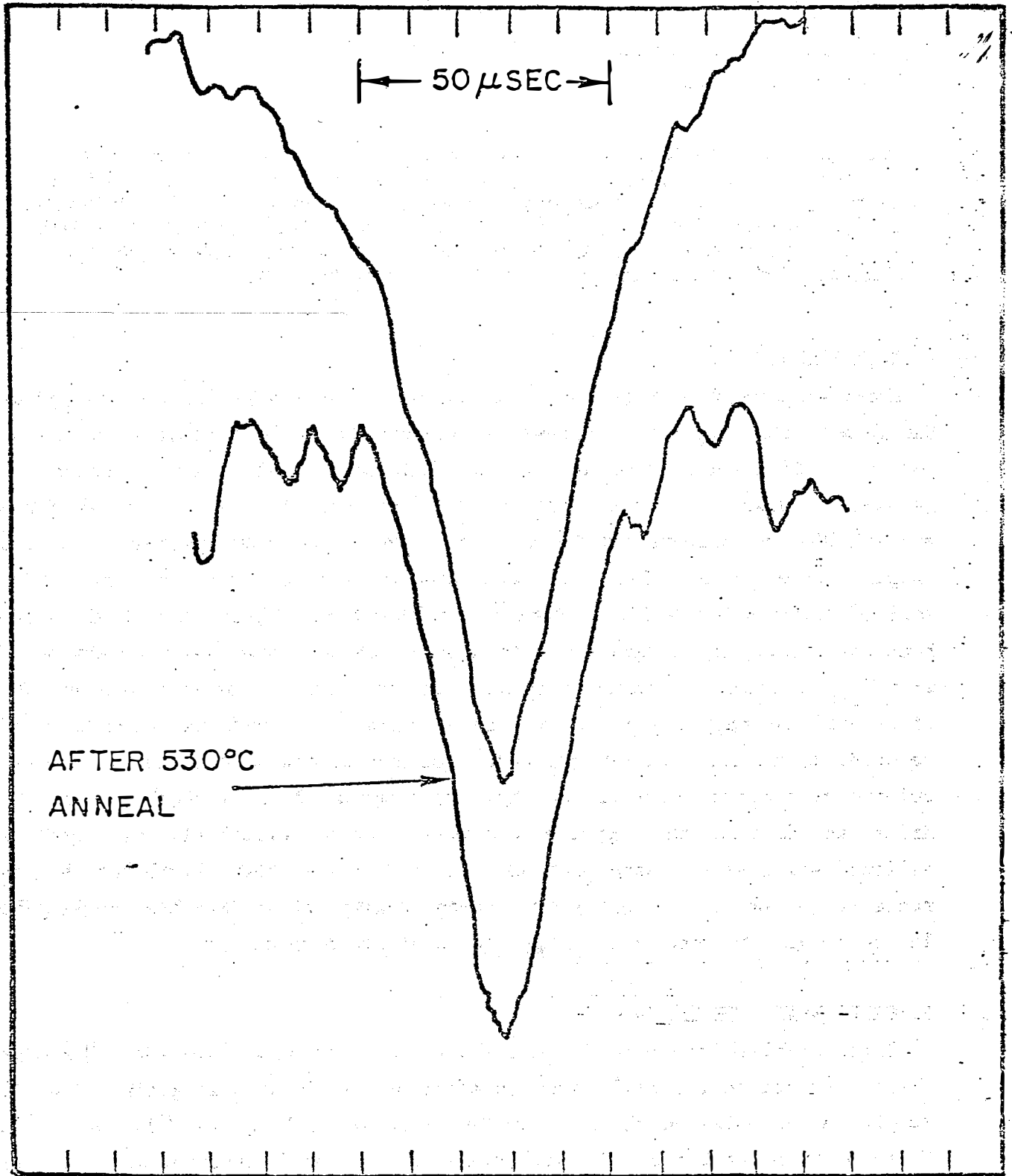


Fig 3

THE ANNEALING BEHAVIOR OF THE $g=2.0026$ ESR LINE IN $a\text{-Si:H}$

W. E. CARLOS

Naval Research Laboratory
Washington, DC 20375

The ESR line at $g=2.0026$ is shown to be due to carbon incorporated into the $a\text{-Si:H}$ film during the deposition process. Results for different films, both doped and undoped, give similar results. The annealing results suggest that this resonance is due to a dangling bond on a carbon atom. It is also seen that contamination from vacuum pumps can give a similar signal which can mask the Si dangling bond line.

1. INTRODUCTION

Electron Spin Resonance (ESR) has proved to be a powerful tool for probing the defect structure of amorphous semiconductors.¹ Although most of the ESR work in $a\text{-Si:H}$ has focused on the trivalent silicon atom with a resonance at $g=2.0055$, a number of other centers have also been observed. Lines at $g=2.013$ and $g=2.004$ are observed in heavily boron doped and heavily phosphorous doped samples respectively. These are attributed to band tail states² or possibly to twofold coordinated silicon atoms.³ In addition, defects due to impurities such as nitrogen, oxygen and transition metals have been observed. In $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films a strong resonance at $g=2.003$ is observed and has been attributed to dangling bonds on carbon atoms.⁴ Dersch and coworkers have reported a similar line at $g=2.0028$ ⁵ and speculated that it could be due to defects at internal surfaces but have reported no detailed work on this line. Miller and Haneman⁶ have reported a similar line on various crystals, including silicon, which were crushed and annealed in vacuum. They attributed the resonance to carbon introduced by hydrocarbon contamination from the vacuum pumps. In their work the resonance disappeared upon exposure to air.

2. EXPERIMENTAL TECHNIQUES

Three samples were used in this study. One, obtained from the IBM Research Center, contained 0.7 at.% boron in addition to ~10 at.% hydrogen. Two other samples were obtained from Brookhaven National Laboratory (BNL1 and BNL2). Both of these contained ~10 at.% boron and 0.6 at.% phosphorous. All three samples were deposited onto hot substrates (~270°C). Samples BNL2 and IBM were deposited onto aluminum substrates which were then removed using dilute HCl. Sample BNL1 was deposited onto a quartz substrate and was left on the substrate

during measurements. No significant sample to sample variations were seen in the specific results reported here.

Most anneals were performed under vacuum using a diffusion pump with a cold trap which was cleaned prior to these experiments and kept cold throughout the course of this work to prevent contamination from pump oils. In addition, some anneals were made in a helium atmosphere to again check for possible contamination. Results for the two annealing procedures were virtually identical confirming that the results were not due to simple contamination during the annealing procedure.

The ESR spectra were taken using a standard Varian spectrometer at resonant frequencies of 35 GHz and 9.3 GHz. Measurements were generally made at room temperature as no change in the lineshape was observed on cooling to 77K.

3. RESULTS

The spectra before annealing and after two different annealing temperatures are shown in Fig. 1. There are two lines present; one at $g=2.0055$ due to silicon dangling bonds and a second sharper line at $g=2.0026$ which is the primary focus of this paper. It should be noted that the small shifts in the positions of the lines are due to changes in the resonant frequency of the cavity and not to changes in the g -values of the resonances. It is seen that the $g=2.0026$ line is present even before annealing but that its intensity is significantly increased by annealing.

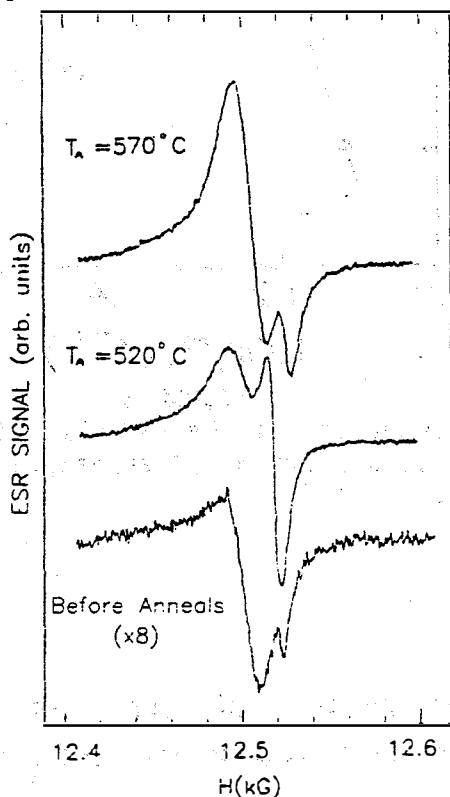


FIGURE 1
The central portion of the ESR spectrum before annealing and after annealing for 20 min. at the indicated temperature. The broader line is at $g=2.0055$ and the narrow line, at the higher field, is at $g=2.0026$

In Fig. 2 the spectra at resonant frequencies of 35 GHz and 9.3 GHz are compared. As has been shown by Dersch and coworkers,⁵ the $g=2.0055$ line is inhomogeneously broadened due to a distribution in g -values and therefore its linewidth is proportional to frequency. The $g=2.0026$ line is however basically a homogeneously broadened line and hence its linewidth is nearly independent of resonant frequency.

As shown in Fig. 1, the intensity of this line is strongly affected by annealing temperature. This is shown in detail in Fig. 3 which gives the intensity of this line as a function of annealing temperature. Extension of the low temperature portion of the curve to room temperature gives a good fit with the before annealing results and yields an activation energy of about 0.2 eV. On the high temperature side, the curve is much steeper and while there are too few data to determine whether the process is activated, a straight line through the points gives an activation energy of about 2 eV.

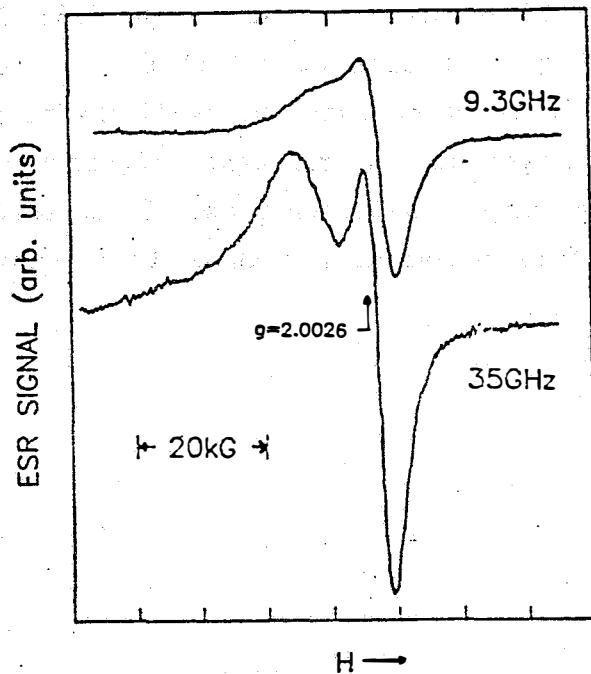


FIGURE 2

The ESR spectrum of one sample (IBM) after annealing to 500°C at two different frequencies. Note that the narrow line width is not a strong function of frequency.

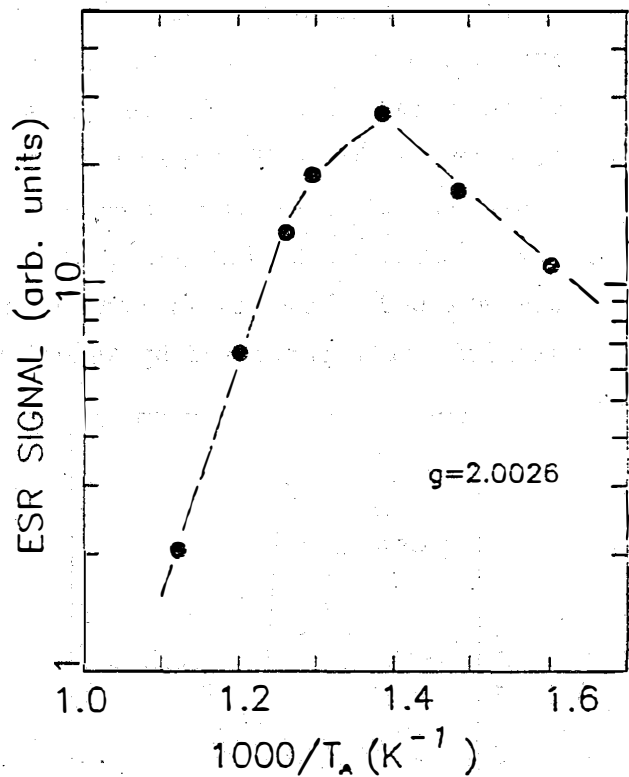


FIGURE 3

The intensity of the $g=2.0026$ line in BNL2 as a function of annealing temperature.

4. DISCUSSION

There are several models to consider for the $g=2.0026$ line. Two possible intrinsic defects are a negatively charged divalent silicon atom and a dangling

bond at an internal surface. However, one would not expect neither defect to yield a homogeneously broadened line such as is seen here. Furthermore, this same defect is seen in a-Ge:H,⁷ clearly indicating that this resonance line is due to an impurity atom.

The most obvious candidate for this center is carbon. Typical glow discharge films contain 10^{19} to 10^{20} carbon atoms per cc.⁸ while the maximum signal seen by ESR is on the order of 5×10^{17} centers per cc. Furthermore, as mentioned previously, a similar line is seen in a-Si_xC_{1-x}:H alloys⁴ and has been associated with a dangling bond on a carbon atom. For atoms with small atomic number such as carbon the spin-orbit coupling, which shifts the g-value from the free electron value of 2.0023, is small, so it is difficult to distinguish one carbon center from another solely on the basis of the g-value.

From the work of Miller and Haneman,⁶ it is seen that a similar resonance appears in samples of crushed materials heated in vacuum. They argue that the resonance is due to hydrocarbons adsorbed on the material and cracked during heating. However, in their work the resonance was not detectable after exposure to air, while in the present study the signal is quite stable even after exposure to air for several days. It therefore seems reasonable to conclude that the carbon has been incorporated into the bulk of the film during deposition. From the annealing data it seems likely that as the sample is heated C-H bonds are broken releasing hydrogen and creating paramagnetic centers. A similar activation energy is seen for hydrogen evolution from a-Si-H.⁹ The sharp drop in the number of centers would then be due to a reconstruction process taking place before the sample actually crystallizes at about 600°C.

As a final note of caution it should be pointed out that a signal similar to this is easily induced in samples sealed in a tube or annealed in a poor vacuum. This is due to contamination, as in the case of Miller and Haneman,⁶ and can lead to spurious effects. As can be seen in Fig. 2, the $g=2.0026$ and the $g=2.0055$ resonances are not easily distinguished at 9 GHz.

ACKNOWLEDGEMENTS

Peter Vanier and J.A. Reimer are thanked for providing the samples used in this work. This work was funded by DOE contract number DE-AC02-80CS83116, administered by SERI.

REFERENCES

- 1) For a recent review of ESR work in amorphous silicon see P.C. Taylor in Semiconductors and Semimetals 21C (in press).
- 2) J.C. Knights, D.K. Biegelsen and I. Solomon, Solid State Commun. 22 (1977) 133.

- 3) D. Adler and F.R. Shapiro, Physica 117B & 118B (1983) 932.
- 4) A. Morimoto, T. Muira, M. Kumeda and T. Shimizu, Jap. J. Appl. Phys. 20 (1981) L833 and Jap. J. Appl. Phys. 21 (1982) L119 and J. Watanabe, Y. Hata, A. Morimoto and T. Shimizu, Jap. J. Appl. Phys. 21 (1982) L613.
- 5) H. Dersch, J. Stuke and J. Beichler, Phys. Status Solidi B105 (1981) 265.
- 6) D.J. Miller and D. Haneman, Surf. Sci. 24 (1971) 639.
- 7) M. Stutzmann, private communication.
- 8) C.C. Tsai, J.C. Knights and M.J. Thompson in these proceedings.
- 9) C.C. Tsai, H. Fritzche, M.H. Tanielian, P.J. Gaczi, P.D. Persons and M.A. Vesaghi in Amorphous and Liquid Semiconductors, ed. W.E. Spear (Univ. of Edinburgh, 1977) pp. 339-343.

Document Control Page	1. SERI Report No. SERI/STR-211-2393	2. NTIS Accession No.	3. Recipient's Accession No.
4. Title and Subtitle Studies of Hydrogenated Amorphous Silicon		5. Publication Date July 1984	
7. Author(s) S. G. Bishop, W. E. Carlos		6.	
9. Performing Organization Name and Address Naval Research Laboratory Washington, D. C. 20375		8. Performing Organization Rept. No.	
		10. Project/Task/Work Unit No. 3432.10	
		11. Contract (C) or Grant (G) No. (C) DE-AI02-80CS83116 (G)	
12. Sponsoring Organization Name and Address Solar Energy Research Institute 1617 Cole Boulevard Golden, Colorado 80401		13. Type of Report & Period Covered Technical Report	
15. Supplementary Notes Technical Monitor: Amir Mikhail		14.	
16. Abstract (Limit: 200 words) This report discusses the results of probing the defect structure and bonding of hydrogenated amorphous silicon films using both nuclear magnetic resonance (NMR) and electron spin resonance (ESR). The doping efficiency of boron in a-Si:H was found to be less than 1%, with 90% of the boron in a threefold coordinated state. On the other hand, phosphorus NMR chemical shift measurements yielded a ratio of threefold to fourfold P sites of roughly 4 to 1. Various resonance lines were observed in heavily boron- and phosphorus-doped films and a-SiC:H alloys. These lines were attributed to band tail states on twofold coordinated silicon. In a-SiC:H films, a strong resonance was attributed to dangling bonds on carbon atoms. ESR measurements on low-pressure chemical-vapor-deposited (LPCVD) a-Si:H were performed on samples. The defect density in the bulk of the films was $10^{17}/\text{cc}$ with a factor of 3 increase at the surface of the sample. The ESR spectrum of LPCVD-prepared films was not affected by prolonged exposure to strong light. Microcrystalline silicon samples were also examined. The phosphorus-doped films showed a strong signal from the crystalline material and no resonance from the amorphous matrix. This shows that phosphorus is incorporated in the crystals and is active as a dopant. No signal was recorded from the boron-doped films.			
17. Document Analysis a. Descriptors Amorphous State ; Boron ; Crystal Defects ; Crystal Doping ; Electron Spin Resonance ; Nuclear Magnetic Resonance ; Silicon b. Identifiers/Open-Ended Terms c. UC Categories 63			
18. Availability Statement National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, Virginia 22161		19. No. of Pages 48	
		20. Price A03	