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Spectroscopic Studies of Hydrogenated Amorphous Silicon

Annual Contract Report
March 15, 1984 - March 15, 1985

S. G. Bishop
W. E. Carlos
Naval Research Laboratory
Washington, D.C.

Prepared under Contract No. DE-AI02-80CS83116

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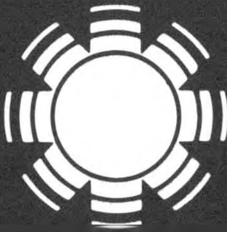

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A Division of Midwest Research Institute

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Executive Summary

Spectroscopic measurements including nuclear manetic resonance (NMR), electron spin resonance (ESR), and photoluminescence (PL) have been performed on hydrogenated amorphous silicon and microcrystalline silicon films grown by a number of SERI subcontractors using various techniques. The overall objective of this work is to provide insights into the structure and electronic properties of these films using probes which are not routinely available.

In the past contract year, ^{1}H NMR has been used to probe the hydrogen bonding in a-Si:H prepared by atmospheric pressure chemical vapor deposiion (APCVD). PL has been used to confirm earlier ESR results that indicated that defects were concentrated near the growth surface of films grown by low pressure chemical vapor deposition (LPCVD). ESR studies of light induced effects in LPCVD films and in microcrystalline films were less fruitful. Only small increases in the number of dangling bonds could be induced by prolonged light exposure. We now believe that this was due to the high dangling bond density before exposure. We were unable to resolve any defects in the microcrystalline films due to boron or phosphorus doping.

In conclusion, ^{1}HNMR has shown us that the hydrogen in APCVD films is more distributed than in glow discharge films. Spin-lattice relaxation measurements may indicate an excessive amount of oxygen in the film studied. Our combined PL/ESR measurements indicate that the top 5000Å of LPCVD grown films has 3-4 times as many defects as the bulk. As mentioned above, we believe that lack of a significant change in the dangling bond density in LPCVD films with light exposure is due to the high initial spin density. With films having a lower defect density this problem should be alleviated.

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1.0 Introduction

The importance in hydrogenated amorphous silicon (a-Si:H) of hydrogen in removing electronic states from the energy gap is well known, but the details of the hydrogen bonding are just becoming available. In addition, the differences in the hydrogen environments for various film deposition techniques such as glow discharge (GD) and thermal chemical vapor deposition (CVD) have not been explored in any detail. One purpose of the present contract is to characterize the local structural environments of hydrogen in CVD films and compare the results to those for GD films. The primary probe used in this work is ^{1}H nuclear magnetic resonance (NMR).

A second significant problem addressed by this work has been the role of intrinsic and extrinsic defects in these films. For this work, electron spin resonance (ESR) and photoluminescence (PL) have been the primary probes.

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 NMR experiments on a-Si:H films prepared by CVD.

2) Use ESR and PL measurements on a-Si:H films.

3) Study light-induced effects using ESR.

4) Study dopants in microcrystalline silicon films.

The films used in this work were obtained from Brookhaven National Laboratory (P. Vanier and F. Kampas), Harvard University (R. Gordon), Chronar (A. Delahoy), and the University of Delaware (R. Rocheleau).

2.0 Fulfillment of Contract Tasks

A. ^{1}H NMR Measurements

NMR studies by Reimer et al.[1,2] and Carlos and Taylor[3,4] have indicated the existence of two distinct hydrogen environments, isolated from each other. These two environments are manifested in the NMR experiments as a narrow (full width at half maximum FWHM ~4 kHz) Lorentzian line superimposed on a broad (FWHM ~25 kHz) Gaussian line. While small sample-to-sample variations are seen in the linewidths, these two NMR lines are present in <u>all</u> reported results. The samples studied have been prepared with a wide variety of different deposition parameters as well as by several different laboratories and still in almost all cases <u>only</u> the two NMR lines representing two different environments are observed. The narrow line can be explained by a distribution of relatively isolated monohydride sites within the silicon lattice while the broad line is attributed to various defect sites such as internal surfaces, and in some films, polyhydride species. Clearly a more precise picture of the

role of different bonding configurations in these two NMR lines is important to a fundamental understanding of the role of the hydrogen in these films.

The spin lattice relaxation time, T_1, of the protons has been studied over a wide temperature range (4K to as high as 800K). All glow discharge films studied have shown a minimum in T_1 at about 30K which is relatively independent of frequency although T_1 is frequency dependent at lower temperatures.[4] Conradi and Norberg[5] proposed a model in which trapped molecular hydrogen molecules act as the relaxation centers. We confirmed this model by observing the ortho to para conversion of the H_2 molecules.[6]

Since that initial observation of molecular hydrogen in a-Si:H, a number of other workers have used probes such as specific heat measurements[7,8] and IR spectroscopy[9,10] to study the molecular hydrogen in these films. Recently, molecular hydrogen has been observed directly using NMR[11]. There has also been the suggestion that the narrow line is partially due to H_2.[12] This has been the subject of some controversy but it is now generally agreed[13] that in typical good quality films, the molecular hydrogen is responsible for only a small fraction of the ^1H NMR line. In atypical films such as those that have been annealed at high temperatures (400°C-500°C) or sputtered in an atmosphere having a high partial pressure of H_2 it is possible to observe motional narrowing of the NMR line as the temperature is increased, indicating the presence of a mobile species. This is illustrated in figure 1 for a film sputtered by W. Paul onto a room temperature substrate using a high partial pressure (5 mTrr) of hydrogen where the narrowing of the line at cryogenic temperatures clearly indicates the pressence of large quantities of H_2 in the film. This is, however, an atypical result and is not observed in good quality GD, sputtered or (as we see below) CVD films.

All of the previous NMR work had been on films prepared by either RF sputtering or glow discharge. A rational extension of our previous work is material prepared by CVD. For the work reported here, we have used a sample prepared by the Harvard group using atmospheric pressure CVD (APCVD). The sample was deposited at 450°C and has an ESR spin density of 3×10^{16} spins/cc.

Several questions have been addressed by the current work, including: 1) How does the NMR line compare to that seen for GD or sputtered films?; 2) Is there an increase in H_2 content as might be expected for films deposited at high temperature?; 3) Is the spin lattice relaxation mechanism similar to that seen in GD films?

Figure 2 shows the ^1H NMR spectrum for the APCVD sample with a typical GD spectra (sample RCA in ref. 4) included for comparison. From the intensity of the NMR line, we calculate that the sample is about 10% hydrogen which agrees reasonably well with the results of other measurements performed by the Harvard group. The spectrum is comprised of narrow (FWHM = 3.8 kHz) Lorentzian line superimposed on a broad Gaussian (FWHM = 19.2 kHz). The two lines are of nearly equal intensity. From the intensity of the narrow line (~5 at %) and its width, we calculate that about 60% of the lattice may be modeled as a random distribution of monohydride bonds. This compares to 40-50% for glow discharge material. The rest of the a-Si:H lattice is comprised of hydrogen-free regions and hydrogen-dressed defects such as internal surfaces which give rise to the broad line.

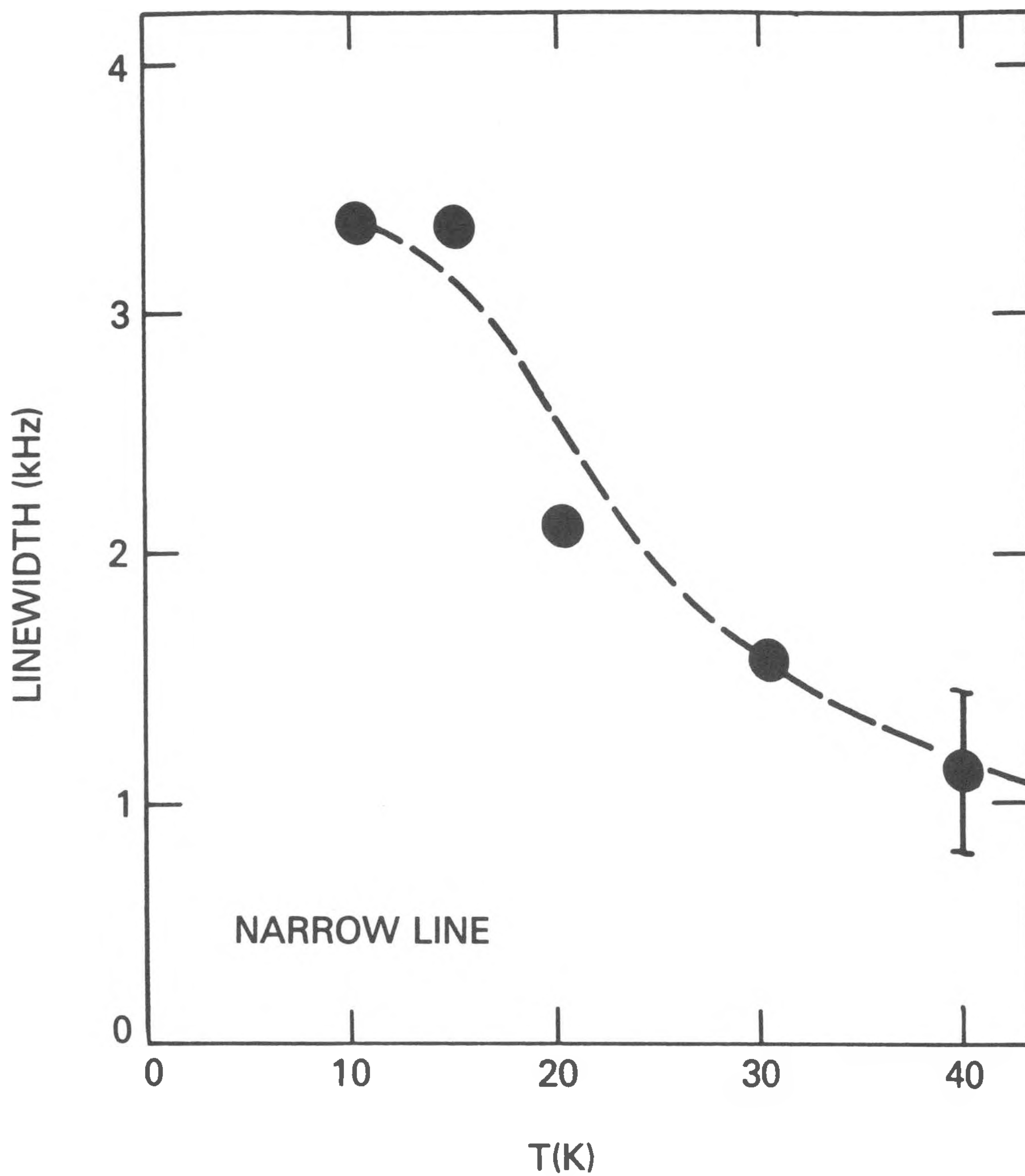

Figure 1. The width of the narrow NMR line as a function of temperature for a film having a high concentration of H_2.

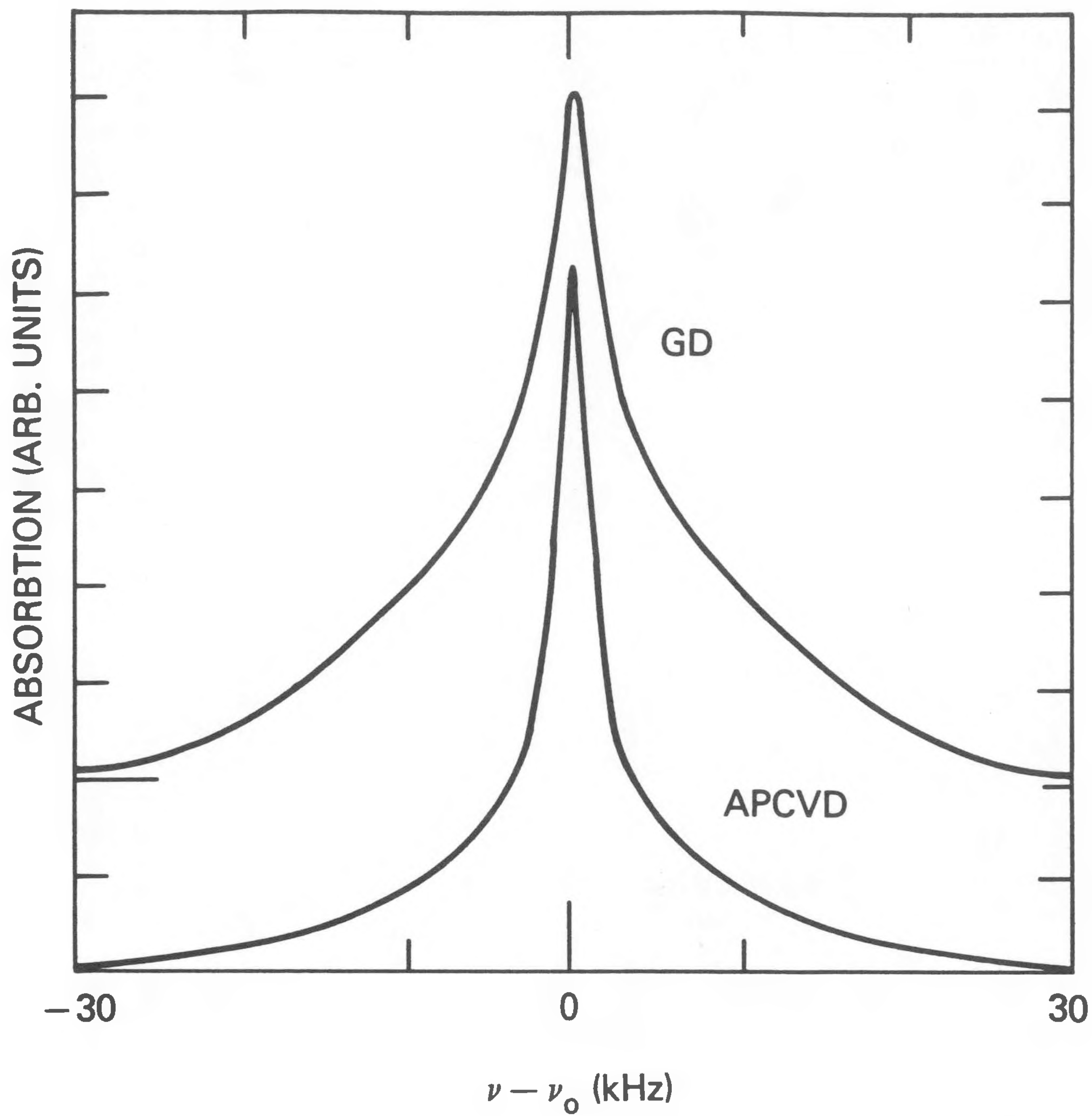

Figure 2. The NMR lines of a typical glow discharge film and one prepared by APCVD.

The lineshape is found to be constant over the temperature range 4K to 300K, clearly indicating that the bulk of the hydrogen is bonded to the lattice, i.e., that H_2 is not a major constituent in the NMR line.

Figure 3 shows the spin lattice relaxation time, T_1, as a function of temperature for the APCVD film and two GD films for comparison. The one GD film is of reasonably high purity (sample RCA in ref. 4) while the other was intentionally doped with ~1.5 at. % oxygen (sample BNL95 in ref. 4). All three films have a minimum in T_1 of about 0.2 sec at $T \approx 30K$. (The ± 50% variation in the values of the minimum is not statistically significant.) The existence of the minimum indicates that there is molecular hydrogen trapped in the films acting as a relaxation center. This minimum is seen for virtually all a-Si:H films. The depth of the minimum indicates that ~1% of the hydrogen in the APCVD film is in the molecular form and acting as a relaxation center (not all of the H_2 is effective as a relaxation center). The lack of motional effects in the NMR line places an upper bound of ~5% on the total amount of hydrogen in the molecular form.

To summarize this point at least 95% of the hydrogen is bonded to the lattice in this APCVD film, while 1-5% is trapped as H_2 molecules. Half of the bonded hydrogen is bonded in isolated monohydride sites while the other half is bonded at defect sites such as internal surfaces.

While all three sets of data in Figure 3 show a T_1 minimum at $T \approx 30K$, the details differ from film to film. T_1 data for higher quality films such as that shown in Fig. 3 (solid circles) show a steep rise in T_1 with decreasing temperature while films with relatively high oxygen content show only a gradual rise in T_1 with decreasing temperature. The APCVD film is clearly similar to the latter group. The temperature dependence of T_1 arises from the relaxation of the H_2 molecule to the lattice. For a two-phonon Raman process one would expect to see $T_1 \propto T^{-7}$. In addition to phonons amorphous materials have low-energy localized excitations known as disorder modes or two-level systems. The energy distribution of these disorder modes is roughly constant in most materials. Raman processes involving disorder modes would then yield a much weaker temperature dependence[14]. Ultrasonic measurements indicate that the number of disorder modes in a-Si increases with increasing oxygen content[15]. This would then indicate that the films having the weak temperature dependence have an increased number of disorder modes, and, given the correlation between disorder mode density and oxygen content, that the APCVD has on the order of ~1 at. % oxygen.

B. ESR and PL Measurements

Both ESR and PL are well established techniques for studying defects in solids. In the case of a-Si:H, Street and coworkers have established that there is an inverse relationship between PL efficiency and ESR spin density[16]. In this work, we have used both techniques to depth profile the silicon dangling bond defects in low pressure CVD prepared films supplied by Chronar and and the University of Delaware. The details of the film preparation and areal spin densities were reported in the previous annual report[17] and are repeated in Table 1 for reference. The Chronar samples were deposited on spectrosil quartz while the Delaware material was deposited on Corning 7059 boro-silicate glass substrates.

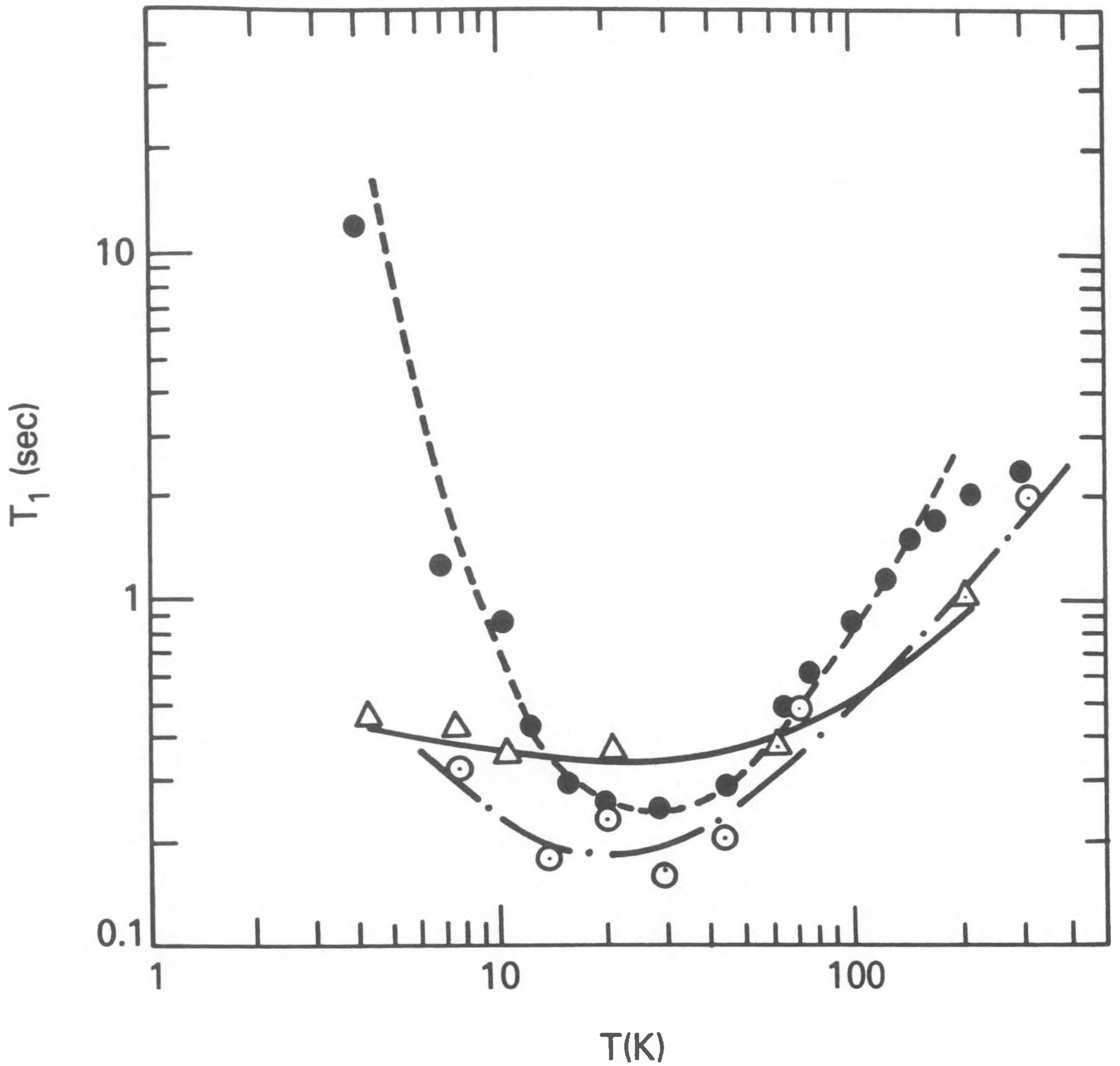

Figure 3. The spin lattice relaxation time (T_1) as a function of temperature from (A) a high quality glow discharge film (solid circles), (B) a GD film containing 1.5 at. % oxygen (triangles) and (C) the APCVD film (open circles).

Table 1. LPCVD Sample Details

Source	#	Pressure (Torr)	Substrate Temp.(°C)	Deposition Rate (Å/S)	Method	Thickness (microns)	Spins/cm^2 ($\times 10^{12}$)
Del.	240-5	24	400	0.5	Flow	1	8
Del.	240-6	24	400	0.7	Flow	1.5	8
Del.	240-7	24	400	0.9	Flow	2	8
Del.	223-C	30	430	1.6	Flow	2	8
Del.	223-D	30	430	1.6	Flow	2	11
Chronar	735	20	470	10	Static	0.5	4
Chronar	736	20	470	10	Static	1	5
Chronar	737	20	470	10	Static	2	6
Chronar	745	20	470	10	Flow	1	5
Chronar	746	20	470	10	Flow	0.5	3
Chronar	747	20	470	10	Flow	2	9

The depth profiling is accomplished by progressively etching away the a-Si:H using a KOH solution. The results of the ESR measurements shown in Figure 4. The ESR spin density is clearly highest near the growth surface.

No increase in spin density is observed near the back interface for either set of samples. As this result runs contrary to the view that the back interface is stressed and has a large number of defects[18], we decided to employ PL as a second probe to study the distribution of defects in these films.

Initially, we had hoped simply to use different wavelengths of excitation light (and hence different penetration depths) to study the depth profile of the defects in these films. This scheme proved intractable and we returned to using the etch back methods. Figure 5 shows typical results comparing the PL intensity before and after removing the top 5000Å of film. The exciting light is highly absorbed, penetrating only about 4000Å of the film. The PL intensity from the bulk of the films is a factor of 5 higher than that from the top layer indicating that the top layer has a higher concentration of defects as was indicated by the ESR measurements.

C. Light Induced Effects

The Stabler-Wronski effect was first observed as a decrease in photoconductivity[19] after prolonged exposure to strong illumination. This effect is seen in ESR as an increase in the dangling bond line after exposure to

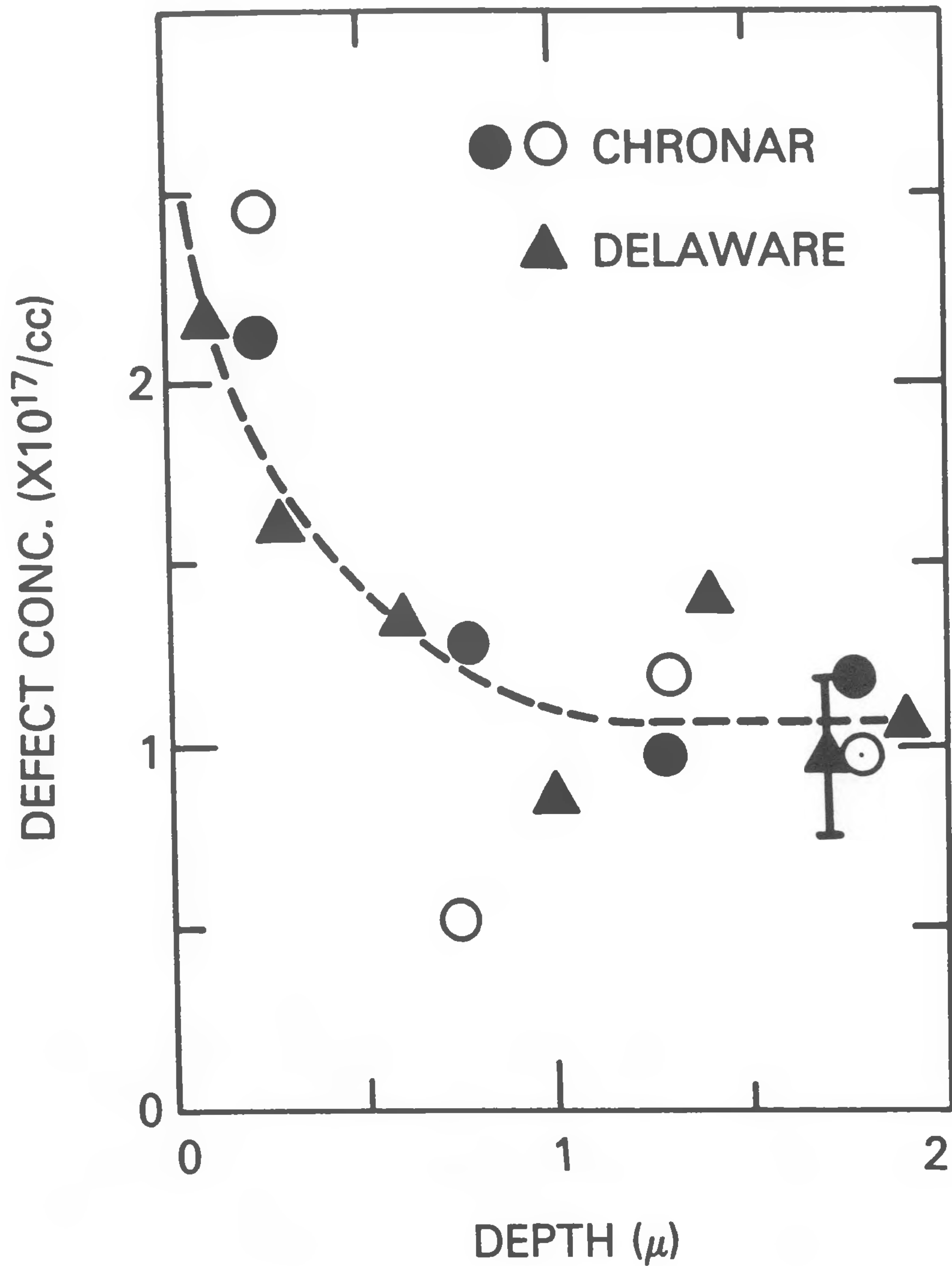

Figure 4. The spin density in 3 LPCVD films as a function of distance from the growth surface. The samples are Chronar 737 (opne circles), Chronar 747 (filled circles), and Delaware 240-7 (triangles).

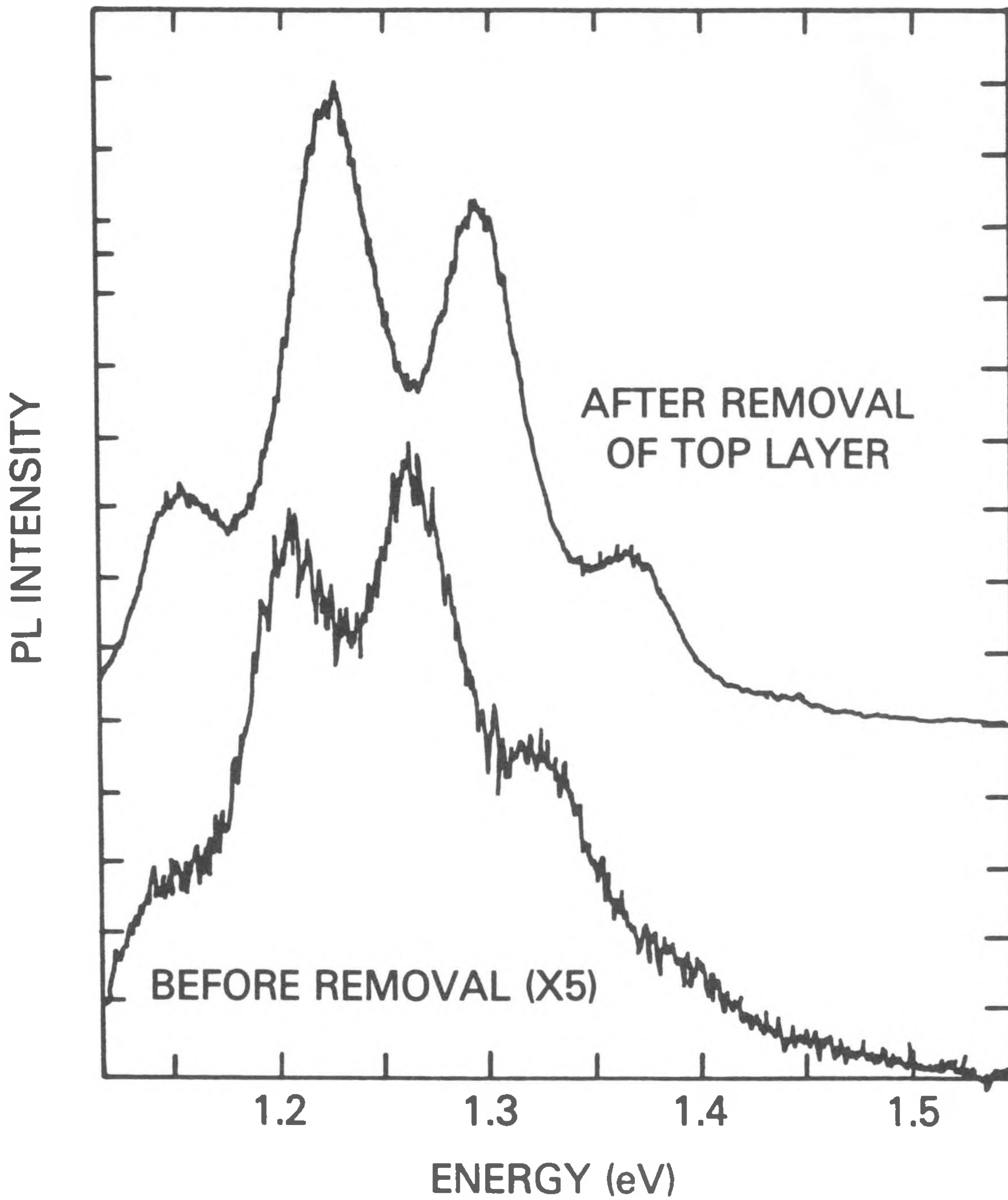

Figure 5. A comparison of photoluminescence intensity for a sample before and after the top 0.5 microns were removed. (The structure is due to interference effects).

light. 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.[20-24] 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.[24] Stutzmann and coworkers[24] have presented data which show the spin density increasing as $(time)^{1/3}$ and have published a kinetic model to explain this result. However, Lee and Taylor[25] have shown the in films with very low ($<10^{16}$/cc) spin density the temporal dependence is even weaker than $t^{1/3}$ as seen by Stutzmann et al.

We have studied LPCVD grown films (Chronar 736, Chronar 745, and Delaware 240-5). The samples were exposed to white light from a tungsten source (100 mW/cm^2) for periods of time up to one month. In all three films the spin density in the film increased by a maximum of 30% to 50%. The small relative changes observed in these samples are primarily due to the high spin densities prior to light exposure. While some improvements in the measurement techniques, such as using a higher light intensity, would enhance the effect, the real improvement must come in the area of higher film quality. The samples used in this work had on the order of 10^{17} spins/cc. If instead they had 10^{16} spins/cc initially the observed change would have been about a factor of ten which might be sufficient to distinguish between $t^{1/3}$ or an even weaker temporal dependence.

D. Studies of Microcrystalline Films

Microcrystalline silicon (μc-Si) is composed of very small (~100Å) 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. Boron and phosphorous doped a-Si:H give distinct ESR lines at $g=2.013$ and $g=2.0043$ respectively. At low temperatures (<30K) crystalline P-doped silicon has a sharp line at $g\cong 1.997$ 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.[25] Boron doped crystalline silicon[26] 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 both B and P-doped films, provided by Brookhaven National Laboratory. The films were deposited by RF glow discharge from dilute silane in hydrogen at an RF power density of 200 w/cm^2 (about 3 times that typically used for a-Si:H). The details on the films are given in table II.

Table II. μc-Si:H Samples

Sample Number	Gas Mixture	Substrate Temperature	Deposition Rate	Thickness	Dark Conductivity
335	$1\%SiH_4+0.04\%\ PH_3$	260°C	1.3Å/s	0.46 μ	$5.2\ \Omega^{-1}\ cm^{-1}$
348	$1\%SiH_4+0.025\%B_2H_6$	165°C	0.9Å/s	0.34 μ	$0.24\Omega^{-1}\ cm^{-1}$
359	$0.25\%SiH_4+0.025\%B_2H_6$	165°C	0.4Å/s	0.15 μ	$1.0\Omega^{-1}\ cm^{-1}$

In the phosphorous doped film only the resonance due to the conduction electrons in the crystalline material is observed. This confirms our preliminary results reported last year.[17] We have been unable to observe any resonance due to band tail states in the amorphous material. We have also looked for phosphorous related defects or donor states in the amorphous matrix, again without success. We therefore conclude that the phosphorous is preferentially incorporated into the microcrystals where it is active as a dopant.

We have studied the two boron doped films in some detail. In particular, we have looked for boron related defects in the amorphous matrix, defects such as interstitial boron in the microcrystals and defects at the amorphous-crystalline interface. Measurements were performed over a range of temperatures (4K to 300K), under intense illumination and after annealing the samples in argon at 250°C. Unfortunately, no ESR signal due to the film could be detected. We must therefore conclude that the boron is incorporated in electrically active sites in the crystaline silicon, although some may also be incorporated in the amorphous matrix in three-fold coordinated sites.

3.0 Conclusions

^{1}H NMR measurements on an APCVD grown a-Si:H film indicate that the hydrogen bonding is quite similar to that in glow discharge prepared films. In addition to the bonded hydrogen, there is a small amount of H_2 trapped in both the APCVD and glow discharge films.

ESR and photoluminescence measurements both indicate that the defect density near the growth surface of LPCVD films is a factor of 3 to 5 higher than the bulk defect density. This damaged layer should be removed before a device is prepared using that region. This could be accomplished by a simple etch procedure or possibly a post-growth anneal.

Efforts to observe increases in ESR spin densities in LPCVD films after prolonged light exposure were unsuccessful due to high initial spin densities. Further work in this area must await improvements in film quality.

ESR measurements on μc-Si:H films indicate that boron and phosphorous are incorparated into the crystalline regions of these films as active dopants.

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