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October 1986

Spectroscopic Studies of Hydrogenated Amorphous Silicon

Annual Contract Report
15 March 1985 - 15 March 1986

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

Prepared under Contract No. DE-AI02-80CS83116

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Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401-3393

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SECTION 1.0

SUMMARY

1.1 OBJECTIVE

The overall objective of this work was to perform fundamental structural and electronic studies of hydrogenated films of Si and Si-Ge alloys and to characterize such materials for other research groups. In all cases, the samples to be investigated were provided by sources outside the Naval Research Laboratory (NRL).

The specific objectives for the period of time covered under this annual report are, (1) to compare light soaking experiments, measured by electron spin resonance (ESR), of films prepared by glow discharge (GD) and photochemical vapor deposition (PCVD) for the purpose of gaining information about the time evolution of the photoinduced defect density and possibly to comment on the relative defect concentration in these two types of films, (2) to perform nuclear magnetic resonance measurements (NMR) on a sample grown by atmospheric pressure chemical vapor deposition (APCVD) in order to identify to what degree this material exhibits a stronger or weaker monohydride NMR signal compared to films prepared by the GD technique, (3) to investigate the ESR and photoluminescence (PL) properties of modulation doped a-Si:H superlattices for the purpose of providing a measure for characterizing the effect of substrate temperature on material quality, (4) to study Si/Ge alloys (provided by Harvard University) by means of PL and ESR techniques for the purpose of identifying the dominant electronic defect in these materials, and (5) to develop a sample/detector suitable for studying time-resolved nonradiative processes in an hydrogenated amorphous alloy film.

1.2 DISCUSSION

The technical discussion of this report is divided into five sections. In Section 2.1 are discussed ESR studies of a-Si:H films. These include characterization (spin counts) of a number of films received from different sources, as well as a comparison of the light soaking effects in two films prepared by glow discharge (GD) and photochemical vapor deposition, respectively. The results are shown to be at variance with a $t^{1/3}$ dependence of the ESR signal on light exposure time t.

NMR studies are discussed in Section 2.2. A brief summary of previous accomplishments under this contract is followed by a discussion of more recent data. The implications of the NMR results for solar cell applications are discussed with reference to past experience regarding the importance of understanding the role of hydrogen bonding in SiO_2 to the improvement of MOSFET (metal oxide semiconductor field effect transistor) devices.

ESR and PL studies of modulation doped a-Si:H superlattices are discussed in Section 2.3. These measurements revealed a definitive dependence on substrate temperature, but no effect on the type of noble gas dilutant. The ESR results correlate with the substrate temperature dependence of persistent photoconductivity measurements which were carried out at another laboratory.

PL and ESR measurements of a-$Si_{1-x}Ge_x$:H:F alloys, prepared by Professor Paul's group at Harvard University, are discussed in Section 2.4. The PL measurements were used to characterize the samples and determine the x value (x ranged from 0.51 to 0.24 over some portions of the sample). Surprisingly, the ESR measurements revealed only a Si dangling bond line but no Ge line. Possible reasons for this observation are given, however, the results are not presently understood.

Finally, in Section 2.5 the successful development of a sample suitable for time-resolved nonradiative studies is outlined. This sample consists of a hydrogenated Si-Ge alloy film which was deposited on a sapphire substrate. A superconducting bolometer was deposited on the other side of the substrate.

1.3 CONCLUSIONS

Most of the conclusions reached in this study are self-evident from the previous discussion. We would like to emphasize the surprising results found for the case of the ESR measurements in Si-Ge alloy films (Section 2.4). These measurements revealed only a Si dangling bond ESR line but no Ge-related ESR signal. This result is in contrast to work by Ishii et al. on similar alloy films in which both Si and Ge related ESR signals were observed. These results can be explained by the possibility that the Ge dangling bond is in a diamagnetic state. Paramagnetism of this state can be induced either by p-type doping, increasing the Ge content, or by application of light with energy near the bandgap of the film. The last option was carried out in this study, however, no Ge dangling bond ESR signal could be observed. Further study of this alloy system for different values of Ge content are recommended.

SECTION 2.0

TECHNICAL DISCUSSION

2.1 ESR STUDIES OF a-Si:H

2.1.1 Light Induced Effects

ESR measurements were made in order to determine metastable light induced effects in a-Si:H. A film prepared by glow discharge (Chronar sample no. D226) was irradiated with a tungsten lamp (total approximate output power ~200 mW//cm^2) for varying lengths of time. The growth of the spin density is plotted in Fig. 2-1 together with the $t^{1/3}$ power dependence which was observed and modelled by Stutzmann et al [1]. As seen in Fig. 2-1, the $t^{1/3}$ behavior does not represent a particularly good fit to the data. In fact, the data are better represented by a functional form such that Intensity (ESR) $\propto$ ln(t).

A second sample studied was a photochemical vapor deposition (PCVD) film (Chronar sample no. G7078). The initial spin density in the dark of this sample was 1×10^{16} spins/cm^3. The magnitude of the light induced ESR, as shown in Fig. 2-2, exhibits a time dependence which is close to $t^{1/3}$ for irradiation times less than ~10 hours, but is seen to saturate at a spin density of ~2×10^{16} cm^{-3} for longer irradiation times.

Stutzmann and coworkers [1] have suggested that the increase in spin density whith exposure to light is due to the breaking of strained Si-Si bonds and that there are ~ 10^{18} - 10^{19} cm^{-3} of such bonds in their samples. This implies that the induced ESR signal would not saturate until that level of defect concentration had been reached. The lower saturated level of the induced signal for the PCVD material compared to GD material may indicate that there are fewer strained bonds (by a factor of five) in films prepared by the PCVD compared to the GD method.

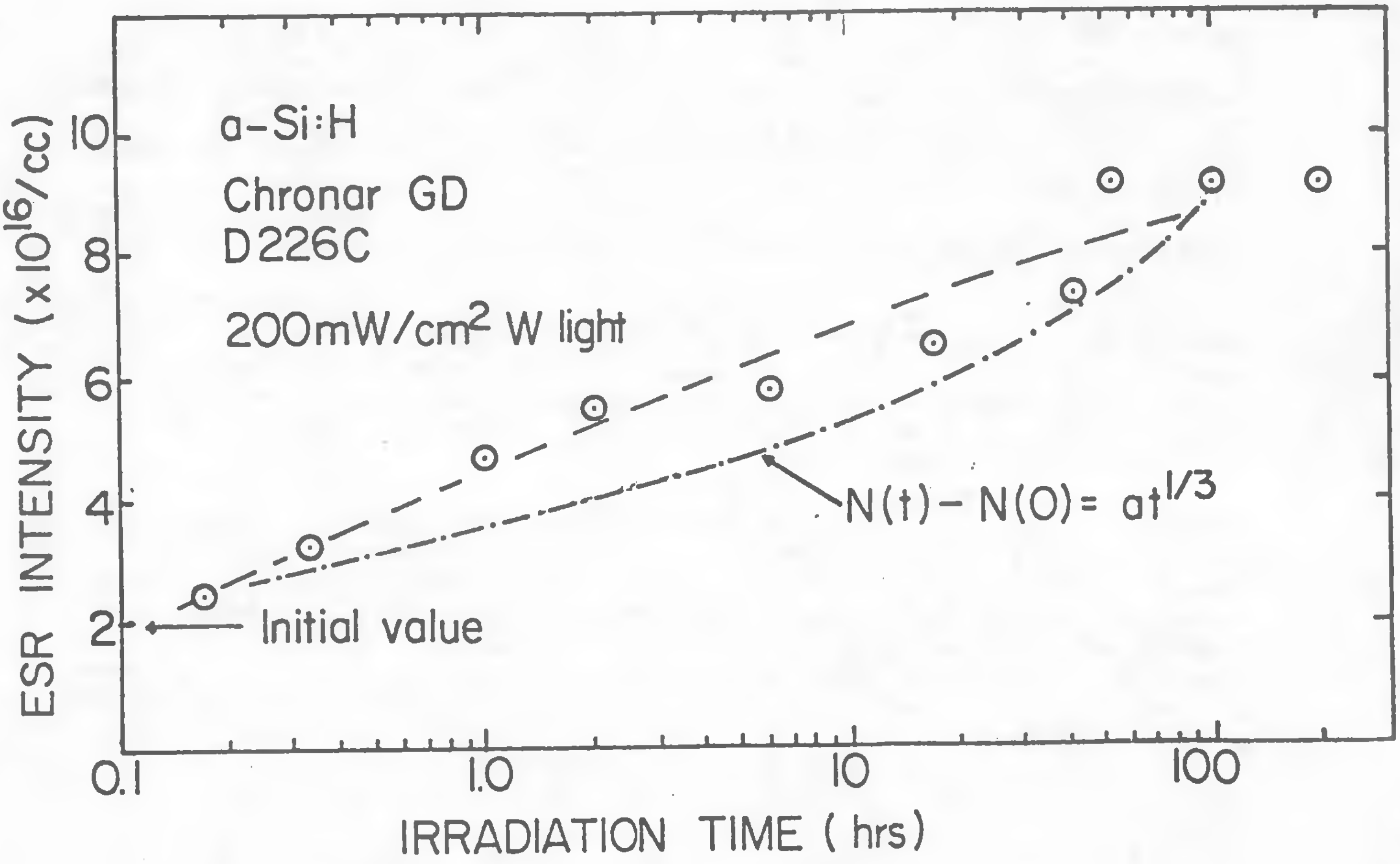

Figure 2-1. Induced ESR at 25°C of an a-Si:H Film. Dashed-dotted Curve is Prediction of $t^{1/3}$ Behavior with $N(0) = 2 \times 10^{16}$ spins cm^{-3} and $a = 1.57 \times 10^{16}$ cm^{-3} $t^{-1/3}$.

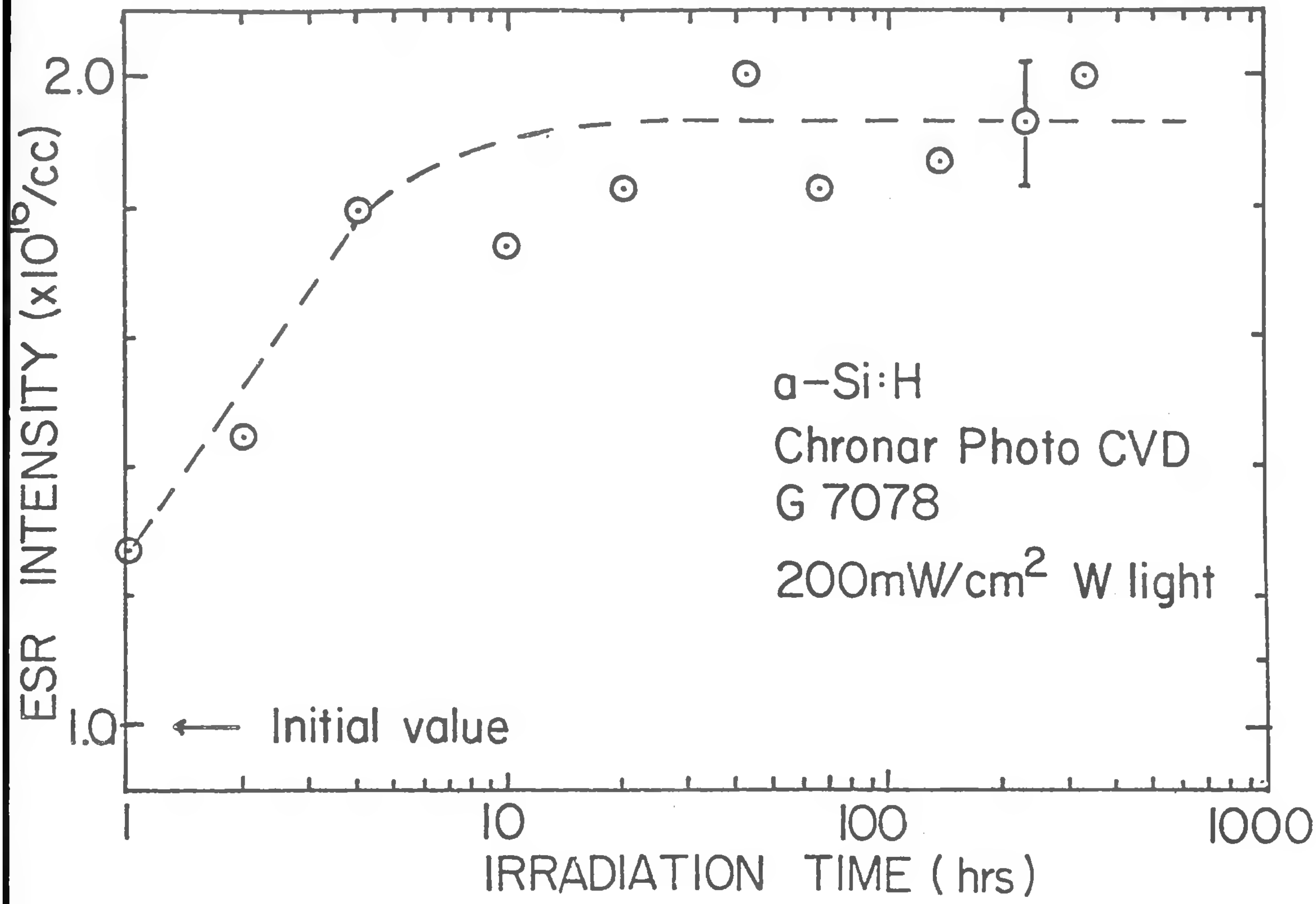

Figure 2-2. Light Induced ESR at 25°C of an a-Si:H Film

2.1.2 Material Characterization

At the request of SERI, routine dark spin counts were performed on a series of a-Si:H films supplied by various manufacturers, in order to assist SERI in evaluations of those materials. The results are summarized in Table 2-1. While it is difficult to make an evaluation of films produced by a particular process and using only ESR measurements, we may tentatively conclude that the defect density in the PCVD films is comparable to and may actually be lower than that in good glow discharge films.

Table 2-1. ESR Results

Supplier	Number	Method	Gas	T_{substr} °C	Spin Count cm^{-3}
BNL	DC60	GD	SiH_4	190	$8x10^{16}$
BNL	DC63	GD	SiH_4	264	$2x10^{16}$
BNL	DC65	GD	SiH_4	320	$5x10^{16}$
BNL	DC49	GD	SiH_4	183	$5x10^{16}$
BNL	DC51	GD	SiH_4	260	$1x10^{16}$
BNL	DC53	GD	SiH_4	315	$3x10^{16}$
BNL	387	GD	SiH_4+H	260	$<1x10^{16}$
Chronar	G7078	PCVD	Si_2H_4	220	$1x10^{16}$
Chronar	G8095	PCVD	Si_2H_6	200	$3x10^{15}$
Chronar	D226C	GD	Si_2H_4	220	$2x10^{16}$
SMU	130	LPCVD	Si_2H_4	500	$1x10^{17}$
SMU	131	LPCVD	Si_2H_4	470	$5x10^{16}$
SMU	271	LPCVD	Si_2H_4	470	$5x10^{16}$

BNL - Brookhaven National Laboratory (P. Vanier)
SMU - Southern Methodist University (T. L. Chu)
GD - RF Glow Discharge
PCVD - Photo Chemical Vapor Deposition
LPCVD - Low Pressure Chemical Vapor Deposition

2.2 NMR STUDIES

2.2.1 Historical Perspective

NMR has provided a number of valuable insights into the structure of a-Si:H films prepared by GD [2-4], RF sputtering [5,6] and CVD [7]. The principal contributions made under this contract in previous years include: (1) The identification of two separate NMR lines due to two different bonding environments [2-4], (2) the first observation of molecular hydrogen in these materials using the temperature dependence of the spin lattice relaxation time [8], and (3) the identification of boron bonding sites as primarily Si_2BH with a minor contribution from Si_3B sites and very little (< 1%) four-fold coordinated boron [9,10].

2.2.2 Recent Results

Recent NMR studies have focused on a sample grown by atmospheric pressure chemical vapor deposition (APCVD) by R. Gordon at Harvard. Substantial progress on this work was completed during the last reporting period and included in the previous annual report [7]. Consequently, the results will be only briefly summarized here.

The sample, which was deposited at 450°C, had a dark ESR spin density of 3×10^{16} spins/cm^3. The NMR spectra were comprised of two lines, as is commonly observed in samples prepared by other techniques. However, this particular sample had a stronger narrow line component (due to an isolated monohydride species) than is typically seen in samples prepared by GD or sputtering techniques. NMR measurements on GD samples performed at various temperatures (4) and our studies of annealed films (2) lead to the conclusion that the appearance of the stronger narrow line component is due to the relatively high deposition temperature used in this APCVD process.

The spin lattice relaxation time has a minimum at $T \approx 30K$ due to the presence of a small amount of molecular hydrogen trapped in the sample. The temperature dependence at $T = 4K$ and 30K indicates that there may be significant numbers of oxygen-related disorder modes in this material.

2.2.3 Implications for Solar Cell Applications

The importance of understanding the details of H bonding and hence the importance of structural probes such as NMR may be best illustrated by analogy with amorphous SiO_2, both in bulk and thin film forms. In a-SiO_2 traps may be formed by exposure to bandgap or subbandgap light (somewhat like the Staebler-Wronski effect in a-Si:H). In SiO_2 films there is ample evidence that hydrogen increases the number of electron [11] and hole traps [12]. In bulk a-SiO_2 the hydrogen concentration affects the number and type of ESR centers induced by subbandgap light [12] and by ionizing radiation [14]. In addition, it has been shown that hydrogen is important for the formation and annealing of defects at the Si-SiO_2 interface [15,16]. Indeed, it may be argued that an understanding of the structural role of hydrogen in Si MOSFETs and in optical fibers has contributed to the dramatic improvements in these devices.

In this context it is reasonable to presume that a detailed understanding of hydrogen bonding in a-Si:H is important to understanding the relationship between the hydrogen bonding in films prepared by different techniques and the light sensitivity of these materials. A specific example might be the improved stability of the photo CVD prepared material. In our NMR work on APCVD films it was found that the isolated (SiH) component was larger in this material than for typical GD material. If this observation carries over to CVD prepared material it may suggest a structural basis for the improved light stability.

2.3 STUDIES OF MODULATION DOPED a-Si:H SUPERLATTICES

The purpose of this study was to compare certain amorphous doped superlattice samples as a function of deposition conditions with PL and ESR techniques. Ten a-Si:H modulation doped samples in film form were investigated. The samples were supplied by Peter E. Vanier from Brookhaven National Laboratory. The films had been deposited on Corning 7059 glass slides and consisted of 12 n-type doped layers 20 nm thick which were alternated with an equal number of 30 nm thick p-type layers. The sample preparation was similar to that described in Reference 17, except for the following details:
For eight of the samples the silane was not diluted with hydrogen or with a noble gas and the substrate temperature was varied from 50 to 400°C; for the other two films argon and helium were used as dilutents at the usual substrate temperature T_s of 250°C. PL and ESR measurements were performed on all of these films and described below.

2.3.1 PL Measurements

PL measurements were carried out using the 5145 nm line of an argon laser. The results are shown in Fig. 2-3. The data have not been corrected for PL interference effects. On the basis of the observed signal-to-noise ratio these data demonstrate the low PL efficiency of the films deposited at 50 and 100°C. On the other hand, within experimental error ($\pm$ 10%), there is no measurable difference in the efficiencies for the next six samples which were deposited at temperatures ranging from 150 to 400°C (the data for T_s = 200, 300, and 400°C are not shown but exhibit a comparable signal-to-noise ratio as for the samples deposited at T_s = 150, 250, and 350 °C). Similarly, there is no measurable difference of the PL efficiencies for the three samples deposited at 250°C with, variously, no noble gas dilutants, or either argon or helium. This result is surprising since previous NMR and optical studies by Reimer et al. [3,4] on a-Si:H films have shown that dilution of the silane with argon leads to increased clustering of hydrogen in the a-Si:H films and also to an increased defect density. No such effects were noted in the present PL and the subsequently discussed ESR measurements which suggests a different morphology for the modulation doped layers compared to bulk film structures with typical thicknesses of 1 μm or more. A trend similar to that shown in Fig. 2-3 is observed for the PL peak positions (averaged over the interference fringes) as as shown in Fig. 2-4, where the peak positions for films deposited at 50 and 100°C are respectively 10% and 5% lower than those for which $T_s \geqslant 150$°C.

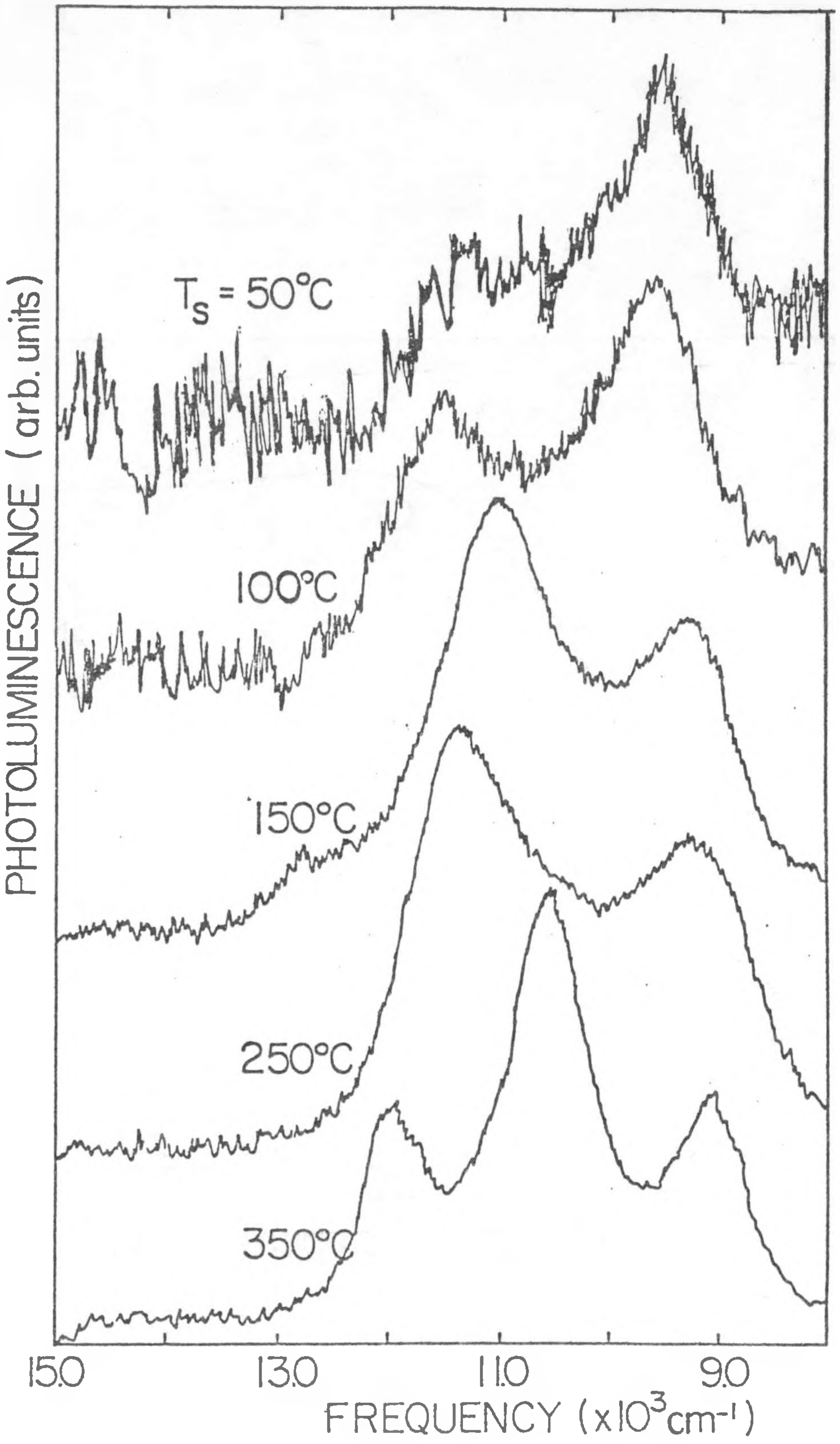

Figure 2-3. PL Measurement of Modulation Doped a-Si:H Superlattices as a Function of Substrate Temperature T_S. Narrow Peaks are Due to Interference Effects. The Samples Referred to in the Figure were Deposited Under Conditions where the Silane was not Diluted with Hydrogen or with a Noble Gas.

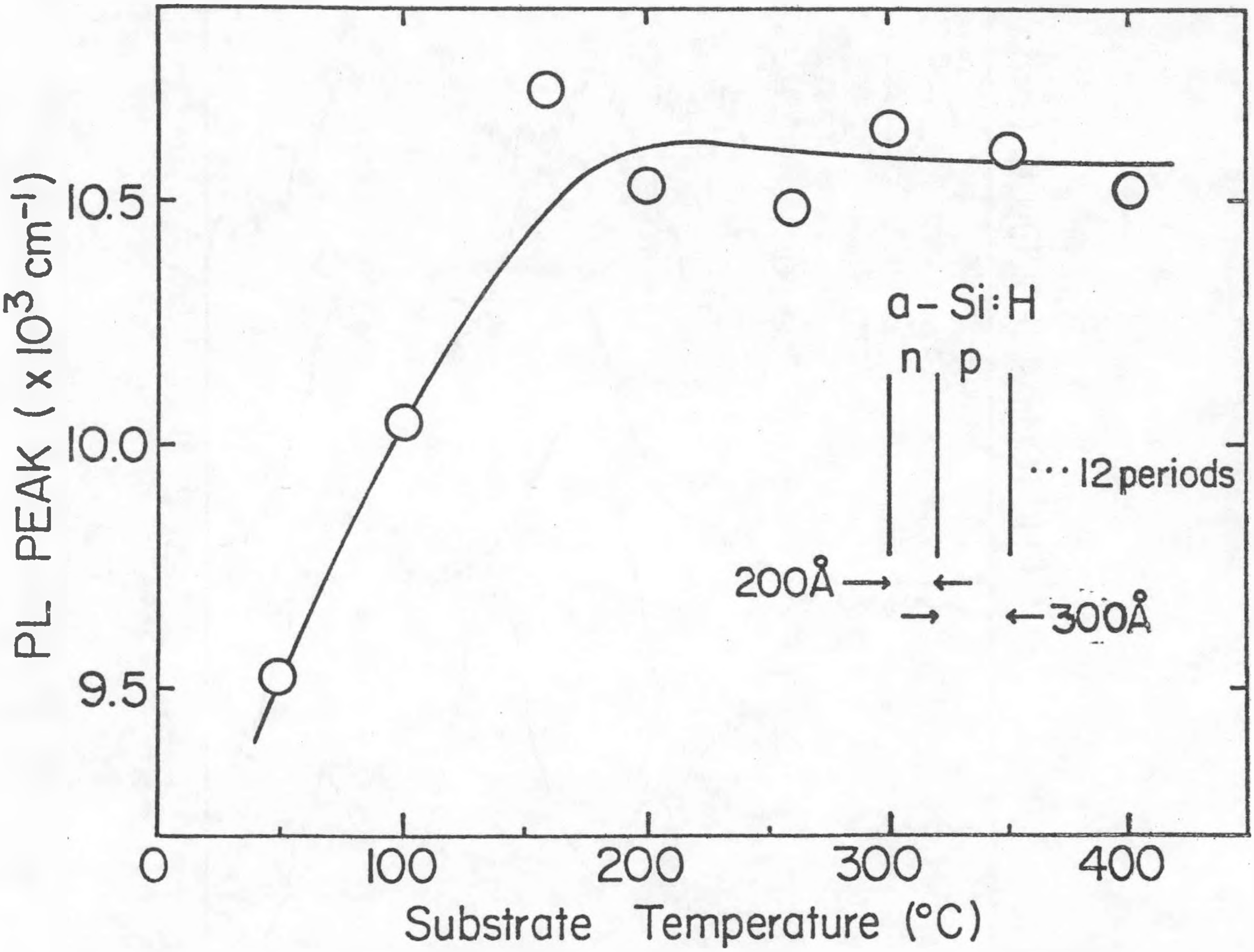

Figure 2-4. Average PL Peak Positions of Modulation Doped a-Si:H Superlattices as Function of Substrate Temperature T_s

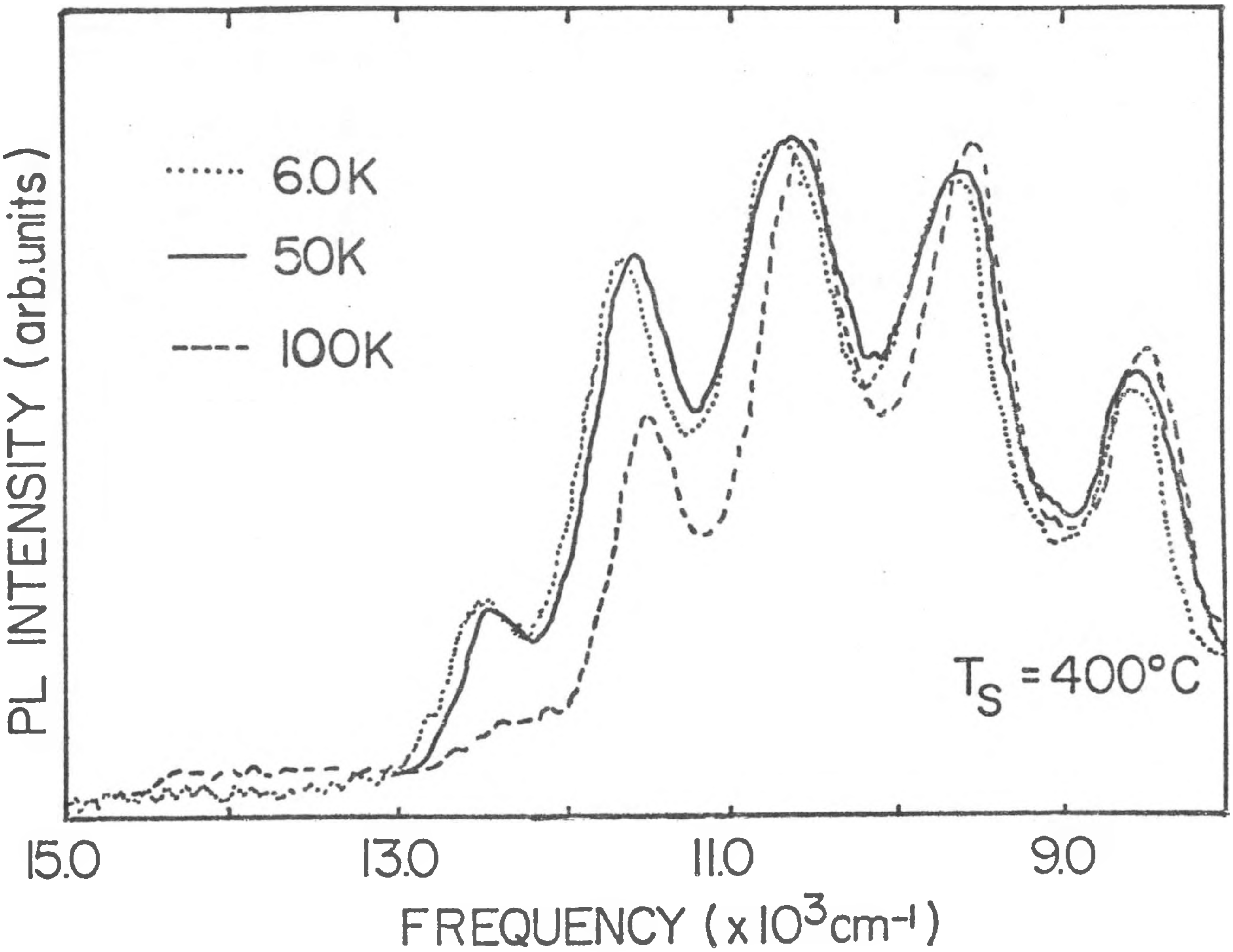

Figure 2-5. Temperature Dependence of PL of a Modulation Doped a-Si:H Superlattice (substrate temperature T_s = 400°C).

PL was also studied as a function of the sample temperature (6.0K, 50K, 100K). The temperature dependence for the film prepared at the substrate temperature of $T_s = 400°C$ is shown in Fig. 2-5. The results are consistent with temperature dependent band gap changes with the PL shifting to lower frequencies with increasing temperature.

2.3.2 ESR Measurements

ESR was measured for each of the ten superlattice samples. A simple spin count for one of these structures is not a useful number. The Fermi level in much of the doped region is near one of the bandedges and so few of the dangling bonds are singly occupied and therefore give no ESR signal. The signal in the dark is dominated by a resonance due to the conduction band tail electrons. Under illumination, the bands flatten out and the dangling bond resonance is again observed. We used the band tail resonance as our standard and measured the ratio of the signal with the light on to the signal with the light off. This will be approximately equal to the ratio of the number of dangling bonds to the number of band tail states. (The number of band tail states is essentially constant from film to film.) The result is shown in Fig. 2-6. As can be seen in the Figure the ratio exhibits a minimum for a substrate temperature of 200°C which is comparable to the substrate temperature at which the minimum persistent photoconductivity is observed [18]. On the other hand, such a change in the electronic properties near 200°C is not evident in the previously discussed PL measurements.

In order to understand these results we offer the following considerations. The optimal deposition in most glow discharge reactors is 200-300°C. At higher temperatures the films have too little H to passivate the dangling bonds, while films deposited at lower temperatures have large amounts of H but also have plasma-induced damage (which anneals out during high temperature growth). Therefore, the minimum in either the persistent photoconductivity or the light induced ESR is seen for films grown at the lower end of the "acceptable" temperature range for growth, i.e. those which probably have relatively high H contents.

In addition, we observed that in these films the doping efficiencies at low substrate temperatures (50 and 100°C) are very poor. The spin-lattice relaxation times increase with exposure to light and may be related to the persistent photoconductivity. No significant differences were seen between the three films grown at 250°C (i.e. grown with either argon, helium or no noble gas dilutant).

2.4 PL AND ESR STUDIES OF a-$Si_{1-x}Ge_x$:H:F

The purpose of this study was to characterize Si-Ge alloys for eventual application in ballistic phonon experiments. Toward this end we have carried out PL and ESR experiments. The material was prepared by Kenneth D. Mackenzie in the laboratory of Prof. William Paul at Harvard University. The film of a-$Si_{1-x}Ge_x$: H:F studied here was deposited on a 3-inch Si disk. The Ge concentration is known to vary significantly over such large dimensions. Consequently PL measurements were made in order to determine the film quality and the distribution of the Ge concentration.

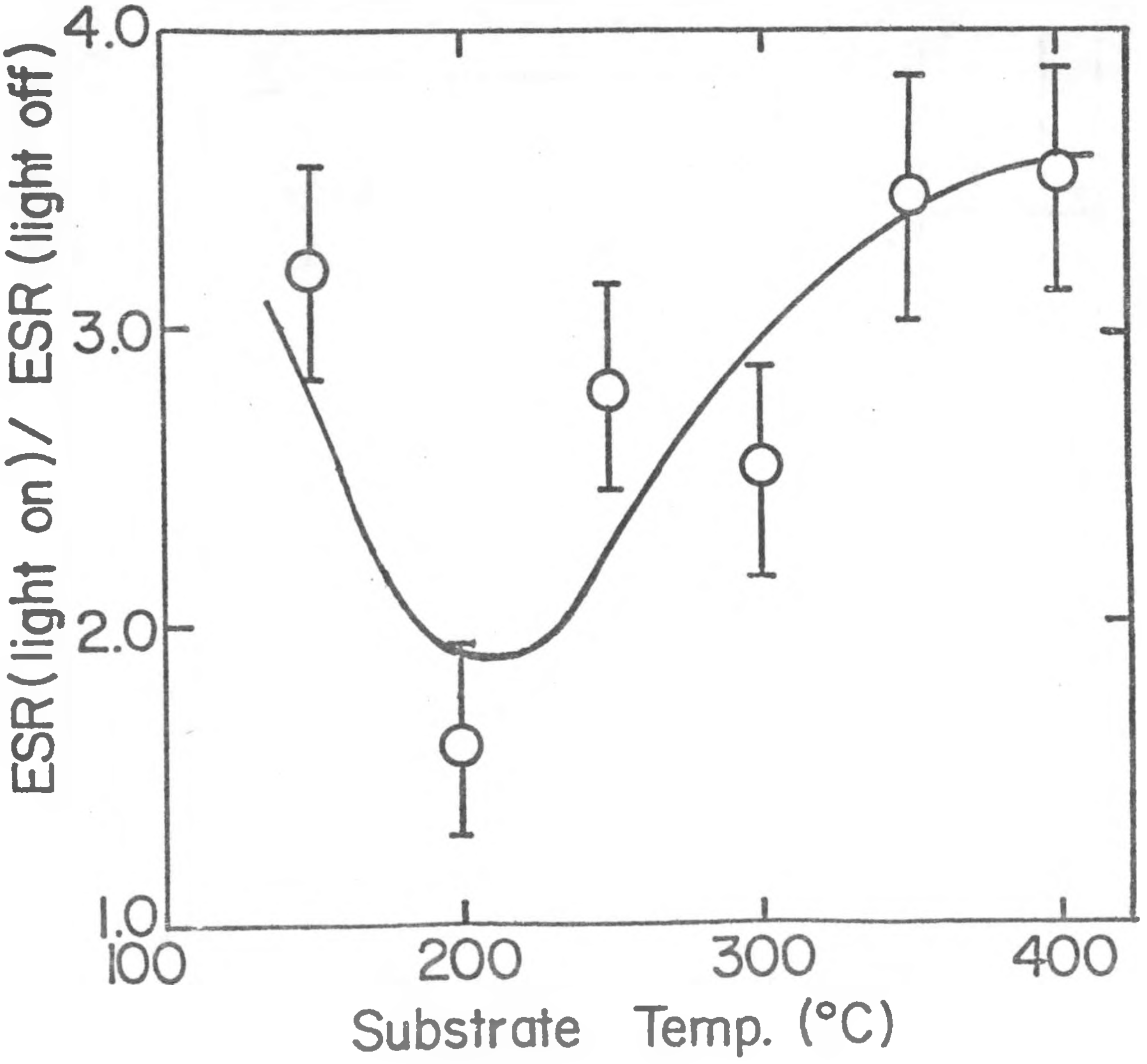

Figure 2-6. Light Induced ESR in Modulation Doped a-Si:H Superlattices as a Function of Substrate Temperature during Deposition.

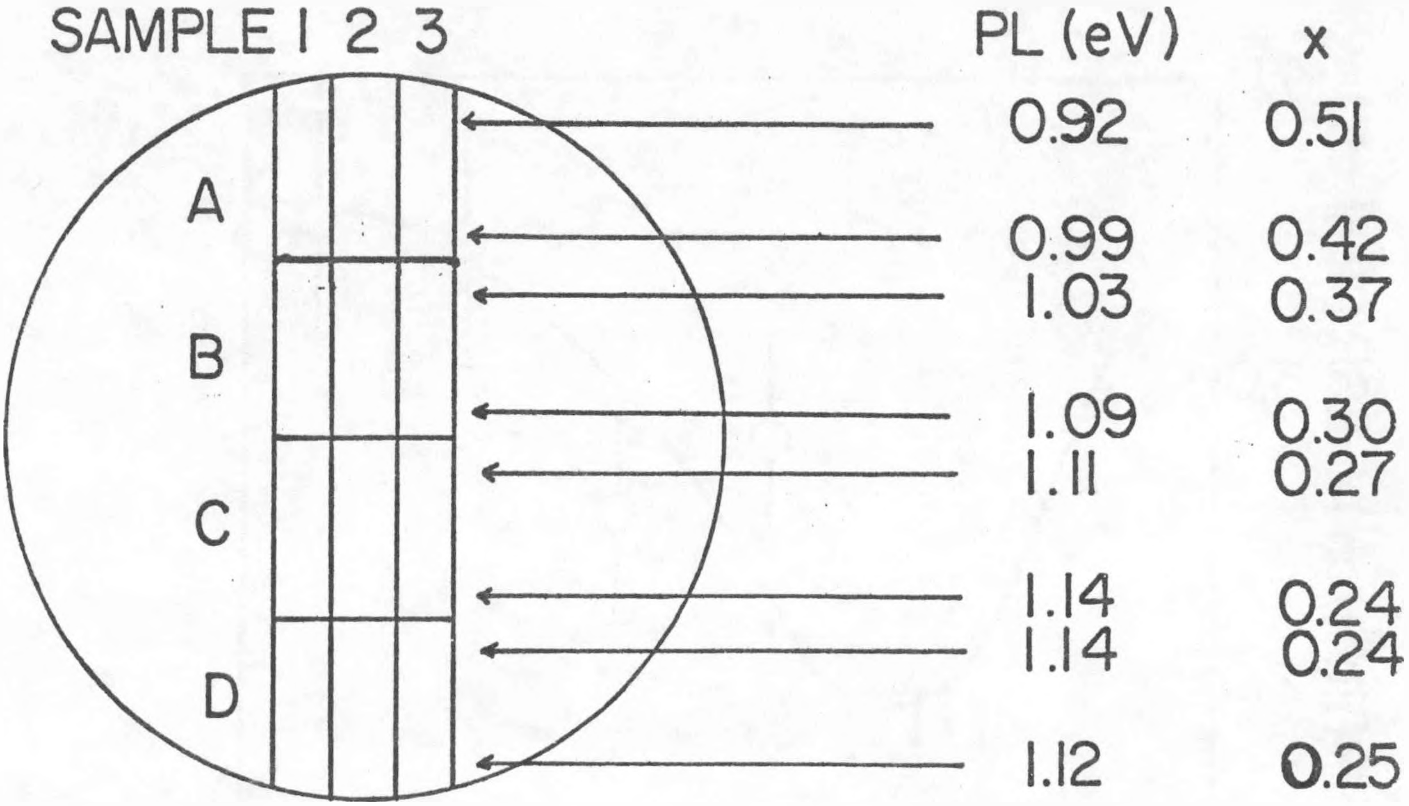

Figure 2-7. Schematic Drawing of 3" Si Wafer Deposited with Thin Film of a-$Si_{1-x}Ge_x$:H:F. Center Section of Wafer was Subdivided into Twelve Samples, as shown.

2.4.1 PL Measurements

The center section of the disk was divided into twelve nearly equal parts, as shown in Fig. 2-7. Using the 5682 Å line of a Kr laser, PL measurements were made near the top and bottom portions of each of the twelve samples. The PL peak positions were found to vary along the long direction of the individual samples. Using a previously determined calibration [19], the Ge content x is determined from the PL peak positions as indicated in Fig. 2-7. The observed changes of the PL magnitude with x were consistent with published results [20].

2.4.2 ESR Measurements

The ESR measurements were carried out using sets of three of the twelve samples which, with reference to Fig. 2-7, were labeled A,B,C,D. The average x values of these samples were 0.47, 0.34, 0.26 and 0.25, respectively. The spectra of samples A-D are shown in Fig. 2-8. The g-value of the ESR lines is near $g = 2.0055$ which has been identified due to Si dangling bonds. No Ge related signal is resolved, which is expected near $g = 2.025$. The lack of a Ge ESR signal is not expected and is in contrast to earlier work [21] in which both Si and Ge related defects were observed in hydrogenated Si-Ge alloy films. Photoemission results indicate that the valence band edges of a-Si and a-Ge are at nearly the same energy, although the band gaps differ by ~ 0.8 eV. Following a simple analogy to a-Si, in which the singly occupied dangling bond is at about mid-gap and the doubly occupied (diamagnetic) state is 0.3-0.4 eV above that, we speculate that in the alloys the energy level for singly and doubly occupied Ge dangling bonds are respectively ~ 0.5 and 0.3 eV lower in energy than the singly occupied Si dangling bond. The Ge dangling bond would then remain diamagnetic until the Fermi level dropped below its two electron level. If this simple picture is correct it is expected to see a Ge dangling bond ESR signal for anyone of these cases: (1) For a Ge rich alloy, (2) for a p-type sample, or (3) using light induced ESR (LESR) in order to produce singly occupied Ge dangling bonds. Because of the unavailability of samples for cases (1) and (2) we used the third method.

The LESR experiments were conducted at T = 4.2K in order to improve the signal to noise level. The results are shown in Fig. 2-9. Within experimental error no light induced ESR signals were measured. The reasons for the absence of LESR in these films are not clear. Possible reasons include an insufficient light intensity (tungsten lamp ~ 100 mW/cm^2) or too rapid a relaxation of any photoinduced charges.

2.5 FEASIBILITY STUDY FOR HEAT TRANSPORT STUDIES IN a-$Si_{1-x}Ge_x$:H

Nearly all spectroscopic studies of a-Si:H are concerned with its electronic and optical properties. However, it has been established recently [22] that there is an interesting correlative relationship which exists between radiative/optical properties (such as luminescence) and nonradiative processes (heat). By studying the time evolution and dependence on laser intensity of both radiative and nonradiative emissions, it was possible to determine the radiative efficiency in a-Si:H films. It was also shown that the thermalization and heat transport in such films are very different for films made from network glasses. It will be of interest to continue these studies in a system of a-Si:H in which the nonradiative efficiency can be readily changed. Such a system is a-Si_{1-x}Ge:H or its fluorinated modifications. It is also of interest to investigate the Staebler-Wronski effect in these alloys as evidenced by changes in the nonradiative transport properties. Toward this end we have, in conjunction with Kenneth Mackenzie of Harvard, investigated the feasibility of a suitable film/insulator/bolometer system. It was determined by Dr. Mackenzie that our original choice a fluorinated Si/Ge alloy film, did not adhere sufficiently well to the sapphire substrate, which was chosen as our insulating sample. Instead, a regular hydrogenated Si/Ge alloy film was deposited on a sapphire crystal. The opposing side of this crystal has a deposited NbN film which is formed in an H pattern. This film is presently anodized to develop a superconducting NbN bolometer which is expected to function at temperatures below 10K.

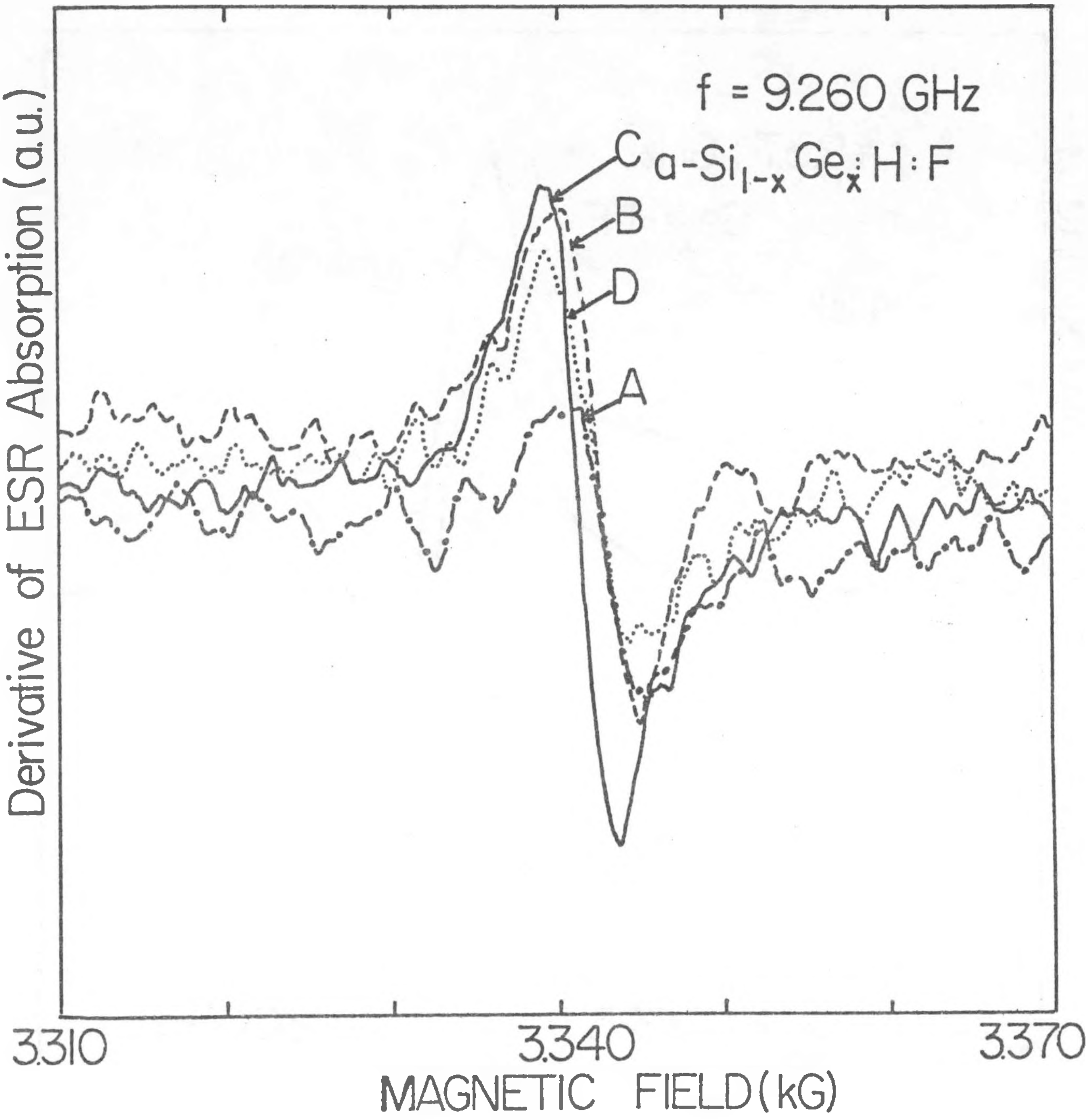

Figure 2-8. ESR Spectra for 4 Films of a-Si$_{1-x}$Ge$_x$:H:F. The Average x Values for Samples A-D are given in Fig. 2-7

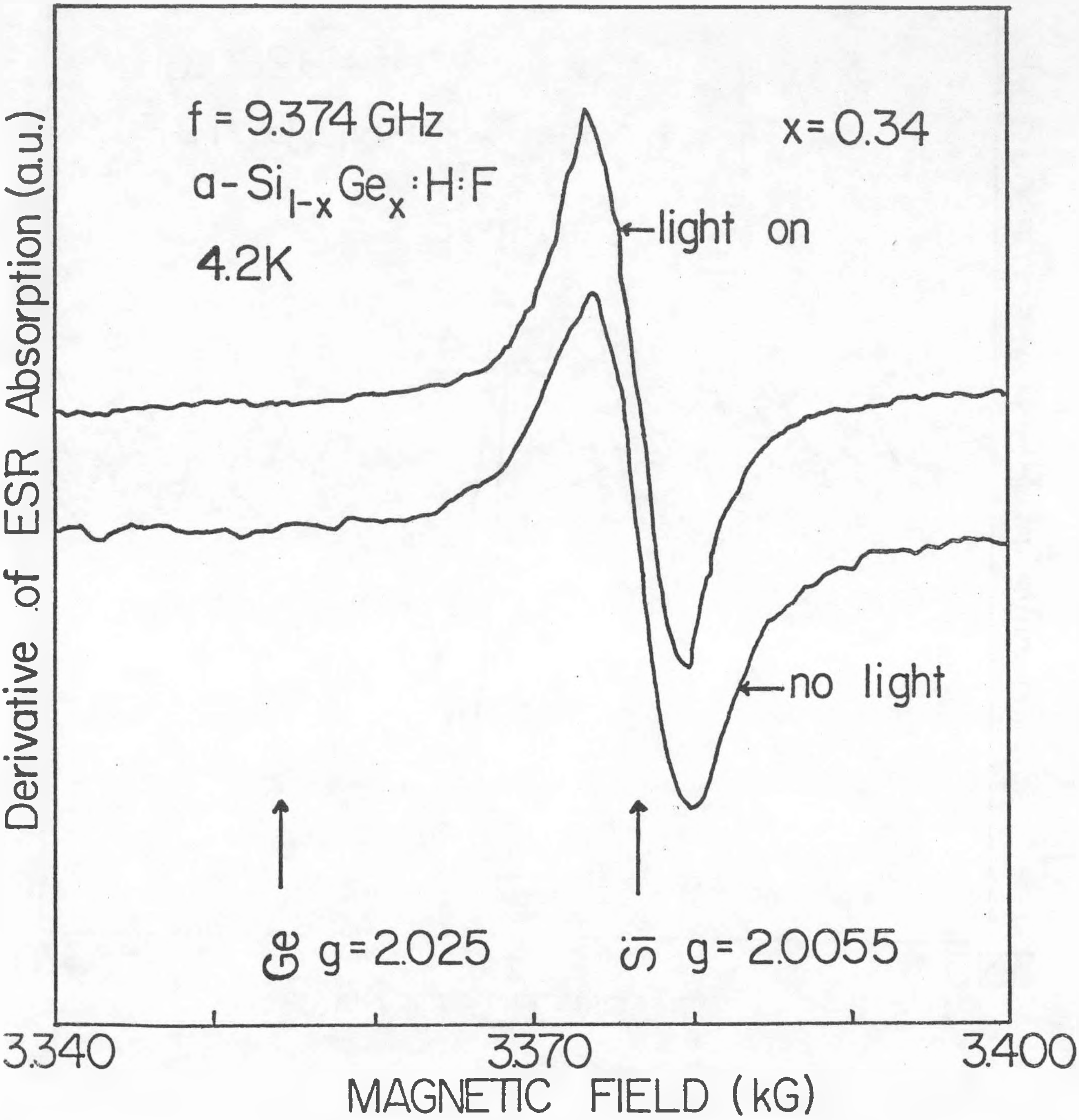

Figure 2-9. Effect of Tungsten Light Irradiation (100 mW/cm^2) on ESR in an a-Si$_{1-x}$Ge$_x$:H:F Film.

SECTION 3.0

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