PHYSICAL REVIEW B VOLUME 18, NUMBER 7 1 OCTOBER 1978

Electron spin resonance of ultrahigh vacuum evaporated amorphous silicon: *In situ* and *ex situ* studies

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(Received 13 June 1977)

An *in situ* study of the electron spin resonance (ESR) of ultrahigh vacuum evaporated amorphous silicon is performed to define the characteristics of the signal as a function of preparation conditions. The influence of deposition rate, temperature of substrates, temperature of annealing, angle of incidence of the vapor beam, contamination by air exposure, and the presence of hydrogen during growth have been investigated. Porosity effects depending on thermal history and angle of incidence, which allow contamination, are observed by ESR. It is found that the spin density is mainly determined by the thermal history and varies only within a factor of about 3 when contamination effects are not involved. This is contrary to other results which we believe were obtained from contaminated specimens. Related variations of linewidth and saturation behavior are observed. *Ex situ* measurements of linewidth, saturation behavior, and ESR susceptibility are done as a function of temperature. The results of these measurements are discussed in terms of two extreme possibilities for spins: individual spins randomly distributed and clusters of spins. The question of a possible association of spins with voids is also discussed. The results are compatible with a model of individual spins randomly distributed. An approach to the relation between spins and conductivity is presented.

I. INTRODUCTION

We report here a study on the dangling-bond electron-spin-resonance (ESR) signal from amorphous silicon (a-Si) prepared by evaporation in ultrahigh vacuum (UHV). We were motivated by the desire to establish the reality of the paramagnetic centers for contaminant-free films and then to give a discussion of their origin and distribution. There are two main reasons for interest in the dangling-bond paramagnetic defects in a-Si. The first reason is the study of phenomena associated with the presence of the defects. For example, these defects may be the hopping sites for variable range hopping conductivity, which itself is of interest as a phenomenon of disordered semiconductors. Another reason is to study the defects as extrinsic centers which can perhaps be removed, so that one might understand intrinsic a-Si without the bothersome effects of defects which can mask, for example, the presence of a possible band gap. Further the defects preclude the controlled study of intentionally added small concentrations of extrinsic centers (doping). For this reason, conventional trace impurity doping of an amorphous semiconductor has been achieved to date only with hydrogenated a-Si which is relatively free of dangling bonds. Both types of studies (intrinsic or extrinsic effects of the defects) require a characterization of the dangling bonds. We present the results below as a contribution to the characterization and understanding of the dangling bonds and their environment in a-Si.

One difficulty concerning amorphous semiconductors is the differences in physical properties measured in various laboratories on materials obtained by different preparation methods and variable conditions within each method. Considerable data is available about effects of preparation conditions, particularly for tetrahedrally coordinated semiconductors.[1-21] Some of the different preparation methods used are evaporation in vacuum, sputtering, ion bombardment, electric plating, and chemical vapor deposition. In each method the influence of substrate temperature, deposition rate, annealing, and the presence of ambient contaminants has to be taken in consideration. In general, the preparation of a-Ge or a-Si introduces extrinsic centers which contribute to the electrical and optical properties. These centers can arise from the presence of impurities introduced during preparation and/or contamination when the sample is exposed to air. In ad-

dition structural defects such as voids have been inferred to exist from ESR, electron microscopy, and small-angle electron and x-ray diffraction[18,22-25] or have been directly observed by electron microscopy.[26-29] Those defects sometimes are assumed to give rise to localized states in the gap which are observable by ESR if the states are singly occupied.

Brodsky and Title[30] found large ESR signals from the group-IV tetrahedrally coordinated amorphous semiconductors Ge, Si, and SiC. Their *a*-Ge and *a*-Si were first prepared by evaporation or rf sputtering and in subsequent work by ion bombardment as well. For these methods of preparation, spin densities of the order of 10^{20} cm^{-3} have been reported. Very different results are obtained in *a*-Si prepared by a glow discharge decomposition of silane where no signal[19,31] or only small signals[32] are observable. From the first studies of Brodsky and Title, *a*-Si is characterized by an ESR signal with an isotropic *g* value of 2.0055. This ESR signal was attributed to dangling bonds by Brodsky *et al.* who showed a qualitative correlation between ESR strength and properties such as optical absorption, refractive index, density, and electrical conductivity.[33-35] The line shape was Lorentzian. In contrast, lines with a partially Gaussian character have been reported from *a*-Si obtained from silane.[32] The dangling bonds responsible for ESR signal were thought to be located in the internal surfaces of voids. This idea was at first suggested by the results of Haneman[36] on the [111] cleaved surface of silicon. Haneman had reported a signal proportional to the area of the [111] surface with the same *g* value of 2.0055 that is found in *a*-Si. Agarwal[37] also gave arguments favoring a surface origin of spins. Small-angle elastic scattering of electrons by Moss and Graczyk[22] supported the idea of voids but more recent work by Shevchik and Paul[24] who studied low-angle x-ray scattering in sputtered, electrolytic, and evaporated *a*-Ge films questioned the quantitative correlation between ESR signal intensity levels and the voids observable by scattering. Similarly the mass density of *a*-Si shows correlation to the spin density only in some cases.[35] Ion implantation studies on silicon have shown that if high enough implantation dose is used, *a*-Si is created with paramagnetic defects also characterized by a Lorentzian ESR line with the same *g* value as *a*-Si prepared by evaporation or sputtering. At lower doses, more varied ESR spectra are seen which can be identified with clusters of vacancies; di-, tri-, tetra-, and pentavacancies have been identified.

All the investigations performed previous to our work were done with *a*-Si samples prepared and/or studied under conditions with less than fully controlled ambient atmospheres. For example, typical evaporation systems used for *a*-Si depositions had base pressures in the 10^{-6}–10^{-7} Torr range and often higher operating pressures leading to possible contamination during deposition at the rate of monolayers per second of residual gases.

Thus we were led to ask several questions about the origin of the ESR signal in *a*-Si. Is it due only to structural defects of the arrangement of silicon atoms or to the presence of impurities? If structural defects are all that are involved, then what are their exact microscopic nature? Are there other structural defects in addition to the ones observable by ESR? To address these questions we have studied the ESR of *a*-Si films prepared by evaporation in very clean conditions. The basic measurements were made *in situ* in order to isolate the effects of contamination. Supplemental measurements were made after the films were removed from vacuum. The *g* value and Lorentzian character of the ESR of evaporated *a*-Si appearing in previous studies to be nearly constant, the only way to get an insight on the nature of spins is to change the characteristics of the ESR. (spin density, linewidth, and relaxation times) that do vary under different preparation conditions. This study includes the analysis of the influence of deposition parameters *in situ*, annealing treatments and contamination by ambients on the strength of the signal. We then give an *ex situ* analysis of linewidth and saturation behavior and their modification with thermal treatments and measuring temperature.

II. EXPERIMENTAL PROCEDURES

Thomas *et al.*[38] have previously described our system which is designed to evaporate silicon in UHV conditions and to measure the ESR signal *in situ*.

The material used for evaporation is a cylindrical rod of very pure nominally undoped silicon. The silicon was obtained from Hobboken and had a room-temperature resistivity of order 1000 Ω cm. This rod is mounted in thermal contact with a water-cooled copper crucible. The diffusion of copper into the silicon is minimized by operating so that only a small part of the silicon is molten during evaporation and the part which is in contact with the crucible remains cold. A Veeco Ve B6 electron gun is used for evaporations. The distance between the source and substrates is 25 cm. The deposition rate varies from ~1 Å s^{-1} to ~150 Å s^{-1}. After several days of outgassing of the whole system, at 200 °C, a base pressure of 1×10^{-10} Torr or less is obtained with a 400 liter s^{-1} ion pump. A titanium sublimation

pump with a liquid-nitrogen trap operates during evaporation. The vacuum is monitored with two gauges, one of them inside the chamber near the substrates. Variations in the composition of residual gases are monitored with a Veeco Ga 4 analyzer. The substrates are polished plates of pure fused silica (dimensions: $10\times 7\times 0.5$ mm); we looked for and found no ESR signal from them. They are chemically and ultrasonically cleaned prior to each pump down. After general outgassing of the entire vacuum system, the substrates are specially outgassed in ultrahigh vacuum at 450 °C for several hours before evaporation. The silicon target is also outgassed for several hours at a pressure lower than 1×10^{-8} Torr. The low-pressure outgassing is to avoid contamination of the silicon melt. These operations serve to limit the outgassing so that the vacuum remained in the range 1×10^{-9} to 3×10^{-8} Torr during evaporation. The higher pressures occur for the fastest evaporation rates. At slow deposition rates (<10 Å s^{-1}), the pressure stays about constant during the whole time of deposition. For faster rates, one can observe a monotonic increase of pressure after a certain time of evaporation. Deposition is systematically stopped when pressure reaches 3×10^{-8} Torr. The time required between the end of an evaporation and the first ESR recording is typically 5 min. *In situ* measurements were done both *in situ* without air exposure of the film after evaporation and after contamination by ambiants.

For the *in situ* experiments, we used an X band ESR spectrometer of local design with 2×10^{11} spins/G sensitivity. The maximum power of the hyperfrequency field was about 20 mW limited by the nature of the microwave source, a Gunn diode. This power was not sufficient to perform saturation measurements *in situ*. After air exposure, all the films were measured *in situ* again and then transferred to an other spectrometer where saturation measurements were performed. The second spectrometer was a Thomson CSF TSN 254 model having a sensivity of 5×10^{10} spins/G and 300-mW maximum power. Both spectrometers used parallelepiped cavities in the TE_{10} mode. For spin-density measurements, we took care to use films with a constant shape and area to insure that the effective radio-frequency field at a given power was constant from one film to another. The precision in the relative measurements is limited by the reproducibility of the position of samples in the cavity. Care was taken to position the samples to within ± 0.25 mm This gives a maximum error in relative measurements of $\sim 5\%$. The absolute number of spins and the g value were determined by comparison with the signal from conduction electrons of crystal silicon. Low temperature measurements were done in a controlled flow of cooled gaseous nitrogen for measurements in the range 100–300 K, or cooled gaseous helium in the range 5–100 K. The experimental line is derivative of the absorption. Peak-to-peak linewidths (ΔHpp) were directly measured or determined from Lorentzian fits to the whole spectra.

We verified whether or not our films were amorphous by examination of Raman scattering spectra obtained from representative samples.[38] This technique is capable of detecting traces of crystallization as small as about 1% of the film volume.

The thicknesses of the films were measured by optical interference fringes based on the Tolanski method. Aluminum was evaporated on several places around the film edge. Thicknesses were then measured on the aluminum-coated steps and the uniformity of the thickness checked at different points. The estimated uncertainties of this method are of the order of 150 Å.

III. *IN SITU* MEASUREMENTS

Preliminary measurements already reported[39] showed that the ESR signal cannot be explained by the presence of impurities in the films; knowing the local pressure near the substrates during evaporation and the deposition rate and assuming a worst-case sticking coefficient of 1 for impurities, we could calculate that the maximum impurity concentration is at least an order-of-magnitude lower than the spin density detected. In addition the sticking coefficient of oxygen to silicon is less than unity at room temperature (RT). So we conclude that the paramagnetic centers which are measured *in situ* in evaporated *a*-Si films are due to defects of the structure. We do not mean to imply that impurities cannot effect the ESR spectrum; in fact we report below on several effects of ambient contamination after film deposition. However, the evidence is overwhelming that the basic observation is that of a silicon broken-bond paramagnetic center. It is with this outlook that we discuss the results below.

The characteristics of the ESR line are similar to those previously reported by others. The g value is 2.0055 ± 0.0002 whatever the preparation conditions. The line shape is Lorentzian or very close to a Lorentzian for films with high densities evaporated on substrates at room temperature (RT) as is shown in Fig. 1. Lines which deviate from a Lorentzian were found for films deposited on heated substrates or annealed (Figs. 2–4).

A. Strength of the signal as a function of preparation conditions

Several published studies report that the ESR intensity can be modified by altering the deposition

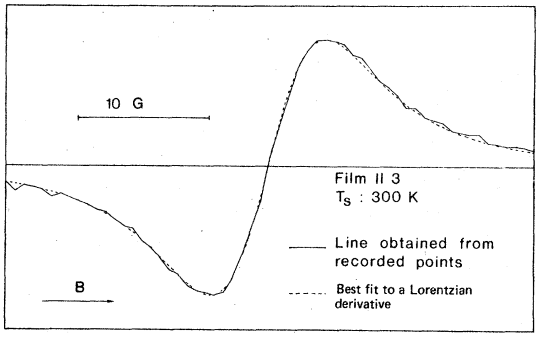

FIG. 1. Comparison of recorded data obtained at RT from a RT deposited sample to the best fit of a Lorentzian derivative computed from the whole data points.

conditions[13,34,35] or subsequent annealing.[2,37,40,41] For instance annealing of films deposited at RT was found to reduce the spin density by more than an order of magnitude. The originality of the present study is to work in the absence of unintentional contamination. This has a marked influence on the results. We have investigated the influence of the thickness, deposition rate, substrate temperature, annealing of films deposited at RT, and the influence of subsequent contamination. The results concerning the spin density of obliquely evaporated films, which were partially reported,[42] are presented further.

1. Influence of thickness and deposition rate

We have measured the spin density as a function

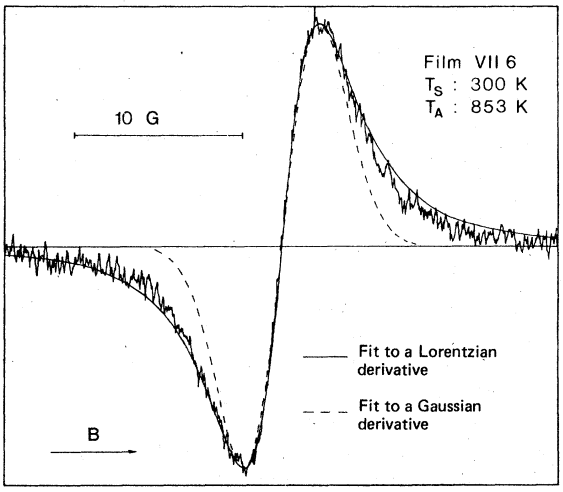

FIG. 2. Line shape of a RT deposited film annealed just below the crystallization temperature is compared to Lorentzian and Gaussian derivative lines of the same peak to peak linewidth. The actual line deviates from a pure Lorentzian line.

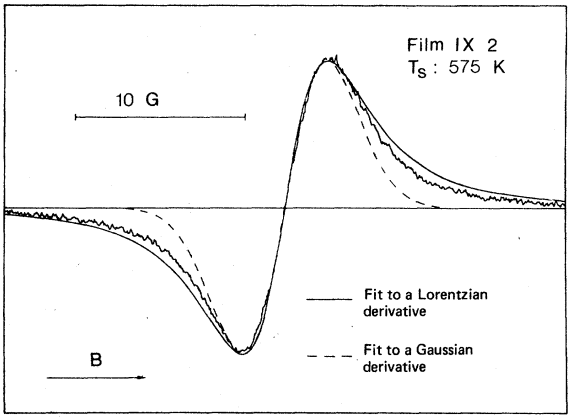

FIG. 3. Line shape of films deposited on heated substrates at high temperature is between Lorentzian and Gaussian derivatives. The line is not strictly symmetric.

of thickness for different deposition rates on films deposited at RT. Three runs, each run consisting of five samples evaporated at the same rate, were made and the results are shown in Fig. 5. In each run, different thicknesses were obtained by successively masking the samples, the evaporation starting at the same time for all samples. This insures the initial-formation conditions are the same for all the samples of the same run. The number of spins scales linearly with the thickness so that the spin density, which is the slope of the line, is uniform throughout the volume and is the same for the three deposition rates 3.5, 13, and 115 Å s^{-1}. In two of the three runs the intercept at zero thickness had a small positive value corresponding to approximately 1×10^{14} spins/cm^2. The proportionality of the signal to the thickness is a general property on which other authors agree

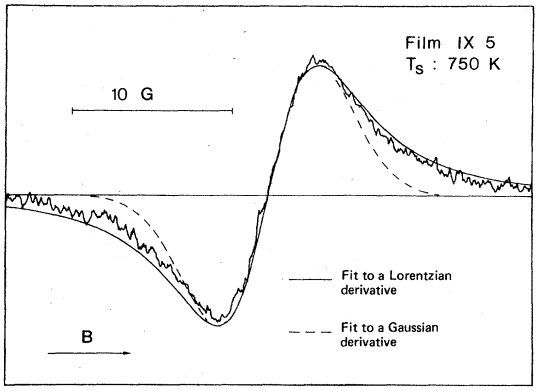

FIG. 4. Line shape obtained from a partially crystallized sample with low spin density is particularly asymmetric.

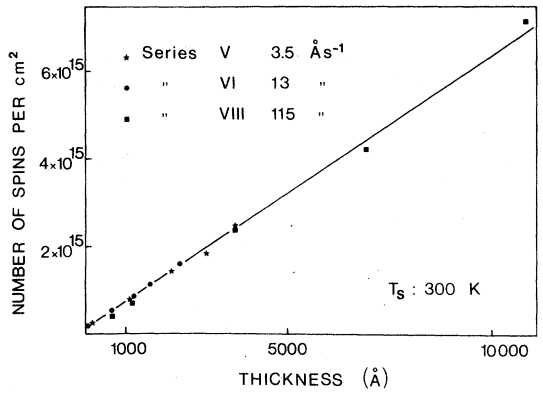

FIG. 5. Number of spins per cm^2 vs thickness for three runs with five samples, each run deposited on RT substrates at different rates. The spin density is constant and is independent of deposition rate.

and which indicates a uniform concentration of defects into the films. For room-temperature substrates and in UHV conditions where contamination is negligible, we do not find a decrease of the number of spins with decreasing deposition rate. This finding is in contrast with other reports. We think a rate-dependent spin density will be found only in conventional vacuum when the contamination rate competes with the deposition rate. However we do find a small deposition rate dependence at higher substrate temperatures T_S. Figure 6 shows the results obtained at $T_S = 380\,°C$, a little below our experimentally determined crystallization temperature limit ($T_S \simeq 430\,°C$). As discussed below some restructuration decreasing the spin density occurs at this temperature. The deposition rate may then compete with the reconstruction rate which would explain the observed dependence. In addition a sharper decrease is observed at very low deposition rates of the order of 1 Å s^{-1} which may be related to the onset of contamination.

2. *Influence of varying the substrate temperature*

Figure 7 shows the variation of ESR spin density with substrate temperature. In this experiment, the deposition rates were all within 20% of each other. As indicated above, the effect of increasing T_S is to decrease the spin density. There is only a factor of 2.2 between the highest density obtained at RT and the lowest density $T_S = 430\,°C$. At still higher substrate temperatures crystallites were found by Raman spectroscopy to be present along with the amorphous phase. Films deposited at or below 430 °C were completely amorphous. The partially crystallized films show a lower spin density than would be expected by extrapolation

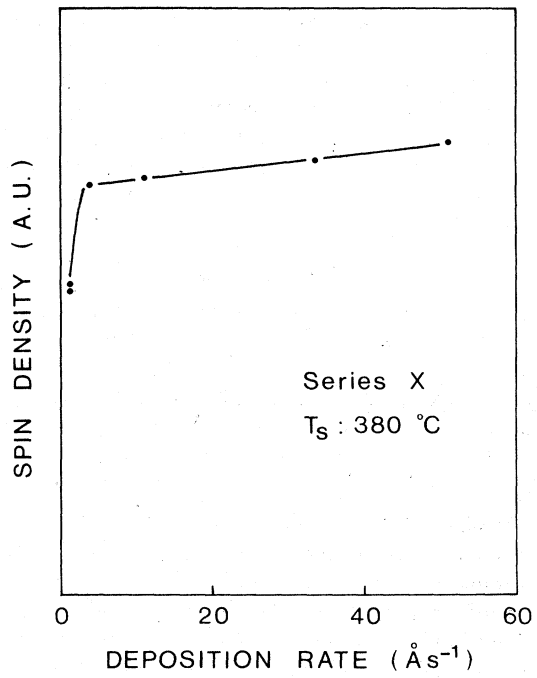

FIG. 6. Spin density vs deposition rate of films condensed on substrates at 380 °C. A slight change of spin density is observed for rates between 3 and 50 Å s^{-1}. An increased change is noticed for rates under 3 Å s^{-1}.

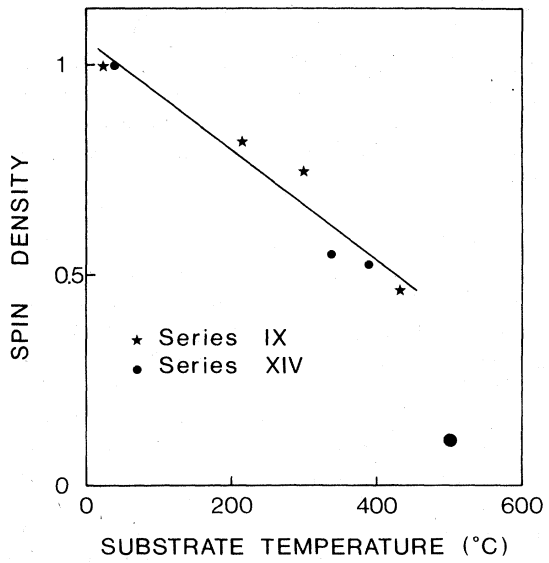

FIG. 7. Spin density vs substrate temperature. The larger black circle refers to a partially crystallized film. Increased dispersion of points may be due to the lack of accuracy of measurements of surface substrate temperature and also to the fact that in these runs deposition rate was not strictly constant for all samples.

of a straight line through the points for the amorphous films. Therefore although we tried, we were not able to use higher temperature substrates and very low deposition rates to obtain useful samples exhibiting a spin density lower than $\sim 3\times 10^{19}$ cm^{-3}. At present it does not appear possible to produce, by evaporation, contamination-free a-Si which is free of structural defects as is conceived for the ideal "continuous random network."[43,44] It appears that the spin density is nearly completely determined by the substrate temperature and that varying the deposition rate has little effect beyond opening the possibility for contamination. We note that Donovan *et al.*[45] have claimed to have produced defect-free a-Ge at high substrate temperatures. However, they did not have the sensitivity to defects that we have with the *in situ* ESR technique.

3. *Influence of annealing*

As we obtain only a small variation of the spin density with T_S in comparison of the annealing effects that was previously reported, we have investigated the influence of annealing on our films evaporated onto substrates held at RT. During the whole experiment the films are kept in UHV. After each anneal the film was cooled and the ESR signal was remeasured at RT. To test the possible modifications due to the successive operations, we have also performed direct anneals (that is no anneals at lower temperatures) at different temperatures of additional films evaporated together at the same time and under the same conditions. The results of these experiments are shown in Fig. 8 where two different experiments of successive anneals and another one of a direct anneal of three different films evaporated at the same time as film VII 1 are represented. The number of spins decreases monotonically with increasing annealing temperature T_A. This reduction is about of a factor of 3.5 after anneal at 560 °C. The two isochronal runs of successive anneals give the same result as direct anneals. Crystallization occurs at about 600 °C. We measured no ESR signal *in situ* from fully crystallized samples. These results are vastly different from those also represented in Fig. 8 previously reported by Brodsky and of those of Agarwal on a-Ge.[37] Their annealing curves show at low annealing temperature (~100–150 °C) an increase of the number of spins followed by a monotonic decrease of the signal by more than an order of magnitude. The strength of the ESR signal was generally not always found to be null after crystallization. We think that these differences must be attributed to impurities and that the present films are less contaminated. It is interesting to note that either

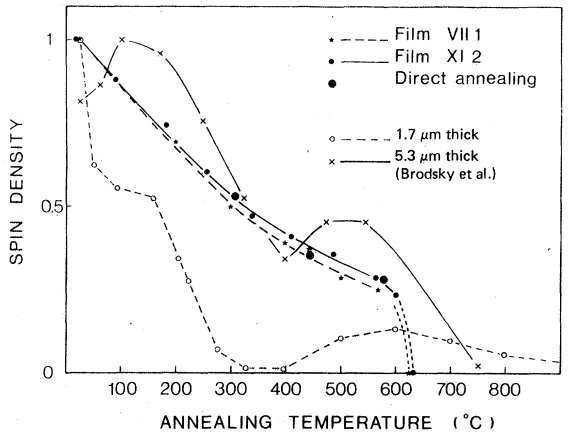

FIG. 8. Influence of successive isochronal anneals of 2 h on the number of spins. Two films deposited at RT at different rates were investigated. Direct anneals of films evaporated at the same time as film VII 1 are also shown. The spin density is reduced by a factor of 4 just before crystallization. After crystallization no ESR signal appears in the scale of the figure. Initial number of spins were normalized to unity. The results obtained by Brodsky *et al*. (Ref. 2) for two films first exposed to air are also shown: thickness-dependent annealing curves are obtained.

growth at T_S (Fig. 7) or an anneal at T_A (Fig. 8) result in approximately the same spin density for $T_S = T_A$, provided UHV conditions are maintained throughout the growth and annealing cycles.

4. *Summary*

It appears that several conclusions may be drawn from this study of the influence of T_S and T_A in spin density.

(a) The fact that crystallized samples exhibit no ESR signal confirms that the signal is due to structural defects and not to impurities.

(b) The monotonic decrease of the spin density with T_A does not seem consistent with the presence of a unique type of structural defects; if such were the case a characteristic temperature would be more likely.

(c) If one disregards the effect of contamination, the spin density is relatively stable: the extreme variation that we obtain is only a factor of about 3 under all preparation conditions.

(d) One result that merits further study concerns the crystallization processes. The sudden drop of spin density during crystallization obtained both with increasing T_S and T_A implies that ESR might be a useful tool for the study of crystallization processes. We are in the process of testing the proportionality of the signal during the first part of crystallization to the remaining amount of amorphous material.

B. Linewidth as a function of preparation conditions

In early work on a-Ge and a-Si it was assumed that the linewidth was independent of preparation conditions and thermal history of the samples. However the linewidths reported by different authors were sometimes different. In recent work on hydrogenated a-Ge,[46,47] or a-Si,[41] it has been shown that preparation conditions influence the linewidth. In our *in situ* measurements we found a strong effect of thermal history on the linewidth. We found the linewidth to be independent of deposition rate, but dependent on substrate temperature T_S and annealing temperature T_A. Figure 9 shows the linewidth measured at low-radio-frequency fields and room temperature of the two isochronally annealed films discussed above and of a series of films evaporated at different T_S. We can see that the linewidth decreases nearly by a factor of 2 upon annealing. A similar result is obtained when one varies T_S. We shall see below that contamination effects can also give a decrease of linewidth, but the fact that similar results are obtained for contaminant-free films evaporated on heated substrates is evidence that structural effects are involved here as well.

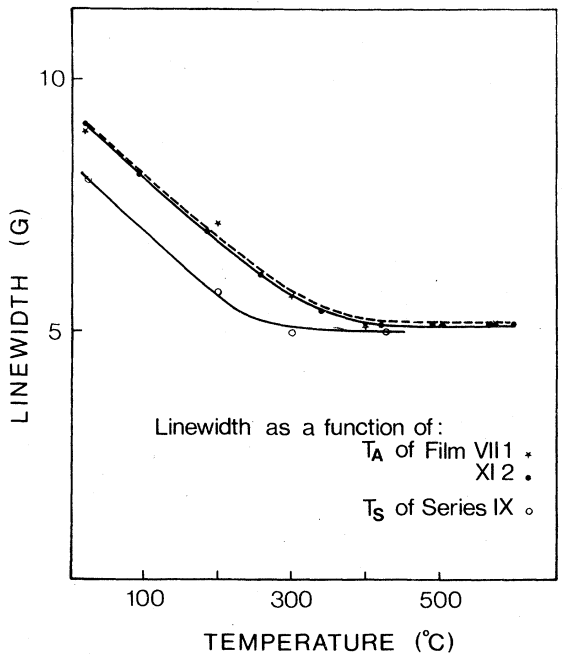

FIG. 9. Peak to peak to peak linewidth measured at RT for films deposited at different substrate temperatures (T_S) or annealed at different temperatures (T_A). Linewidth decreases with increasing T_S at T_A and tends towards values of the order of 5 G.

IV. CONTAMINATION AND RELATED QUESTIONS

Once chemically pure films have been produced, we can study contamination effects on these films. One can distinguish small effects observed after subsequent air exposure. In addition we have grown films at oblique incidence which are highly susceptible to contamination. We have also attempted to contaminate with hydrogen during deposition.

A. Contamination under vacuum

After the first measurements *in situ*, a small change with time of the ESR signal of RT deposited films is noted, expecially on thin films: while the amplitude increases a little, the linewidth decreases and the total number of spins stays about the same within experimental accuracy.

We have also found a thickness dependence of the linewidth for very thin films (<1000 Å) deposited at RT which might be related to contamination. Thin films always exhibit smaller linewidths than thick films. Alternatively there can be a surface contribution to the signal with different characteristics. Only thicker films (>1000 Å) will be considered in what follows.

B. Contamination after air exposure

After air exposure a reduction of spin density and linewidth of RT deposited films is observed. This effect is thickness and pressure dependent. The linewidth as a function of thickness after several weeks of air exposure is shown in Fig. 10. Thin films are more sensitive to contamination than thick films. Exposure to pressures of the order of 10^{-3} Torr has no effect on a time scale of minutes on films thicker than 1500 Å and no effect on the scale of weeks for films thicker than 6000 Å. In the other hand, changes of linewidth

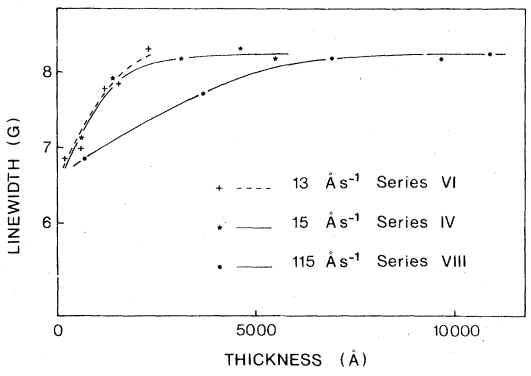

FIG. 10. Influence of thickness on linewidth for different series deposited at different rates at RT. Measurements were done after air exposure. Linewidths tend to values of ~ 8.5 G when thickness increases.

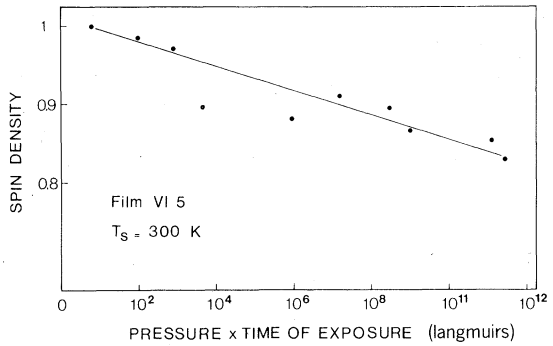

FIG. 11. Spin density of RT deposited films is always found to be decreased by air exposure. This decrease, time and pressure dependent, is consistent with gas diffusion into the film.

were observed after exposure to pressures of 1 at and were found to have the dependence on time and pressure shown in Fig. 11. Contamination effects are not observed on films annealed at high temperature or deposited at high T_S (above ~200°C). We have not performed a precise determination of temperatures T_A or T_S above which films become insensitive to contamination.

We think that these results indicate that air or moisture diffusion into the film is possible at RT. The time-dependent number of spins after air exposure and the dependence with the gas pressure is consistent with a slow diffusion rate of gases. This point of view is supported by results presented below on films evaporated at oblique incidence.

The question of porosity is related to the problem of voids and void shape. Different arguments arising mainly from diffraction, microscopic, and gravimetric measurements have been given in order to establish the existence and shape of voids. Diffusion effects reported above show that one must be very careful about conclusion from gravimetric measurements. For example, if 10 at.% or 20 at.% of a film is oxygen, gravimetric densities should not be compared with crystal densities. These diffusion effects can also explain the large amount of impurities which have been determinated to be present in a-Si films by certain authors. One must also note the fact that a void network which allows gas penetration is evidence for connection between the voids.

In contrast, films evaporated on heated substrates are not readily contaminated, implying isolation of the voids from each other either because of reconstruction or because of a lower concentration of voids.

Knotek[48,49] has obtained evidence for porosity on UHV-grown a-Ge films. He found that oxygen can diffuse quickly across the films in unannealed films and that the diffusion is enhanced by annealing films in presence of a low pressure of O_2. Such contamination effects were not observed on high-T_S deposited films.

To summarize, it appears that RT deposited films are porous so that their properties change with time, whereas films evaporated at high substrate temperatures are insensitive to gas contamination.

C. Influence of oblique incidence

The effect of evaporating Ge films with the plane of substrate at oblique incidence to the Ge vapor was reported to produce samples with different optical, electrical, and structural properties than films deposited at normal incidence.[50-53] The presence of macroscopic defects was observed. Analysis of electrical conductivity data implied that the films were porous. We have measured *in situ* the spin density of films deposited at RT as a function of the angle of incidence between 0° and 60° (Fig. 12). Within experimental accuracy, the spin density is independent of angle. Measurements of the linewidth show a slight linewidth broadening with angle. The effect of air exposure at atmospheric pressure is also shown in Fig. 12 for the 0° and 60° films. A reduction of spin density by a factor of 2.2 of the film evaporated at 60° is observed. This reduction mainly occurs in

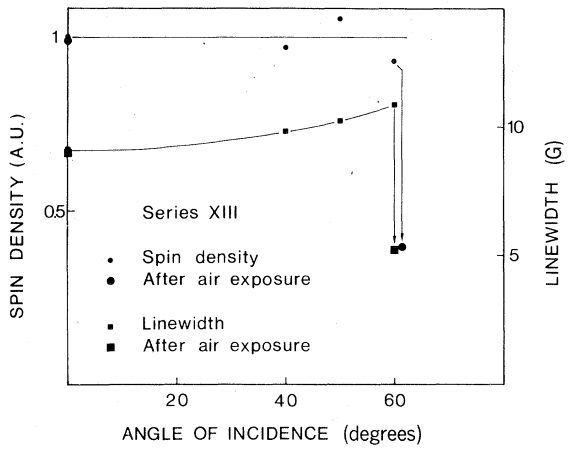

FIG. 12. Spin density of films evaporated at different angle of incidence is constant within experimental precision. After air exposure (~ 2 h), the 60° sample has its spin density reduced by a large factor. The main part of this reduction takes place in the seconds after air exposure. On the contrary, the normal incidence film shows only a very small reduction of spin density. The linewidth increases slightly with angle and is reduced by air exposure. These changes upon air exposure are similar to those observed when one anneals a film deposited at RT. In particular, the 60° film becomes saturatable at RT after air exposure.

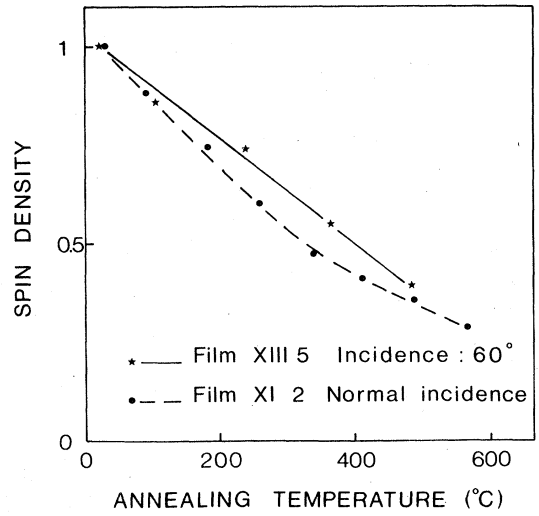

FIG. 13. Behavior, upon isochronal anneals of 2-h, of the spin density of a RT and 60° incidence deposited sample, is compared to the one of a normal incidence film. The variations of spin densities are similar.

the first few seconds after air exposure. In contrast, only a very slight decrease is observed on the 0° film. This is evidence that a bulk contamination due to a strong porosity of the 60° film occurs. Upon air exposure we also observe a strong narrowing of the linewidth of the 60° film. Only a very slight effect is observed on the 0° sample. The spin-density and linewidth reduction effects are accompanied by a change of the saturation behavior of the signal with increasing microwave power: after air exposure, saturation effects are observed at RT on the 60° film.

The *in situ* annealing of a 0° and a 60° film is shown in Fig. 13. The reduction of spin densities upon annealing is similar in both films. This result is additional evidence that *in situ* annealing effects are not due to contamination because we have just established that the 60° film is sensitive to contaminants if any are present.

D. Films grown in presence of hydrogen

Incorporation of hydrogen during growth is known to reduce the spin density of *a*-Ge films[46,47] prepared by sputtering. We searched for effects during evaporation due to molecular hydrogen as well as nascent hydrogen. Nascent hydrogen was produced by passing H_2 over a heated tungsten filament near the substrate. The efficiency of our method as measured with a gas mass analyzer was weak, that is only a small fraction (about 5%) of the molecular hydrogen broke up. In any case no noticeable effect on the spin density was measured even for films grown in a pressure of 5 $\times 10^{-5}$ Torr of hydrogen. This indicates that molecular hydrogen has no effect on spin density and that either the efficiency of this method is not sufficient to produce enough nascent hydrogen to be incorporated into the films, or that some additional mechanism such as ionization is needed to incorporate H into *a*-Si.

V. TEMPERATURE DEPENDENCE

After air exposure, we have studied the ESR characteristics as a function of temperature.

A. Saturation and linewidth

The ESR signal strength as a function of microwave power depends strongly both on preparation conditions and on measuring temperature. Qualitatively, the higher the deposition temperature T_S or annealing temperature T_A, the more saturatable the line is. Also the line becomes rapidly more saturatable as temperature is decreased. However it is generally not possible to associate a definite longitudinal relaxation time T_1 to the saturation characteristics. This is demonstrated in Fig. 14 where the expression $(P^{1/2}/Y'_m)^{2/3}$ is plotted as a function of microwave power P. Here Y'_m is the peak-to-peak signal height of the absorption derivative. If the system were

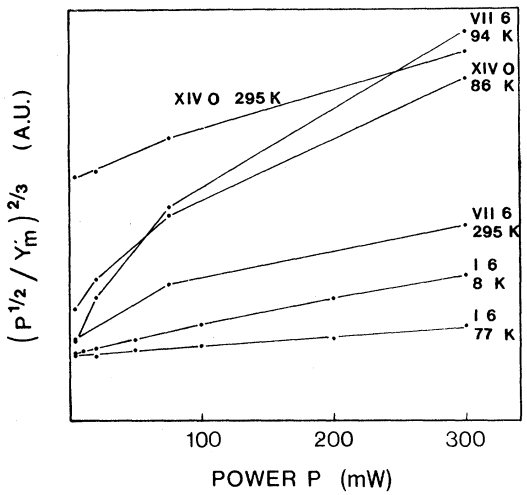

FIG. 14. Plot of $(P^{1/2}/Y'm)^{2/3}$ as a function of power P. $Y'm$ is the peak-to-peak amplitude of the derivative. In the case of a definite T_1 one must obtain a straight line (T_1 is relative to the slope of the line and to the value of the function at zero power). The data obtained for three films measured at different temperatures shown in the figure is represented. Film I 6 was deposited at RT. Film VII 6, deposited at RT, was annealed at 580 °C. Film XIV 0 was deposited at 385 °C. The nonlinearity increases when measuring temperature is decreased.

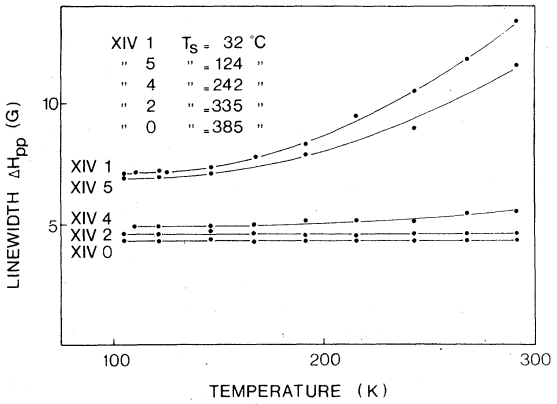

FIG. 15. The linewidths of films deposited at different T_S vs measuring temperature. Two components of the linewidth, temperature dependent and temperature independent, are derived from the data. The temperature-dependent part is very sensitive to T_S.

characterized by a single T_1, the plot would be linear. We find strong deviations from linearity, especially for samples evaporated at high substrate temperatures. This indicates that the line is not homogeneous and not to be characterized by a single longitudinal relaxation time T_1. The RT deposited films which are less easily saturatable (only when measured at low temperatures) also show more nearly linear characteristics. We think that this should be correlated to the higher spin density in these films: generally speaking an increase of interactions among spins will render the line more nearly homogeneous. This is also to be correlated to the variation of lineshape according to preparation conditions presented in Figs. 1–4. Figure 15 shows the temperature dependence of the peak-to-peak linewidth for films deposited at different substrate temperatures T_s. We can divide the measured linewidth into two terms:

$$\Delta H = \Delta H_0 + \Delta H_1(T) .$$

ΔH_0 is the temperature independent part obtained by extrapolation at zero temperature. $\Delta H_1(T)$ is the temperature dependent part. ΔH_0 and ΔH_1 depends differently on preparation conditions. $\Delta H_1(T)$ is strongly dependent on T_S: it becomes null for films with low spin density deposited near crystallization temperature. ΔH_0 is weakly dependent on T_S. It varies by less than a factor of 2. ΔH_0 is due to a pure transverse relaxation process (T_1 process) since ESR is highly saturatable at low temperature with microwave fields of a fraction of gauss. On the other hand $\Delta H_1(T)$ appears to be associated with a longitudinal relaxation mechanism (T_1 process) since it varies with the saturation behavior: e.g., the RT deposited films are not saturatable at RT, where $\Delta H_1 \simeq 3$ G and become saturatable at lower temperatures where ΔH_1 becomes lower than a gauss.

B. ESR susceptibility

To get some information about the interaction between spins, the ESR susceptibility was measured as a function of temperature on RT deposited films. Strong saturation effects at low temperature made it impossible for us to measure precisely the susceptibility at low temperatures for either high-T_S deposited films or annealed films, using the absorption mode. Figure 16 shows the variation of the inverse signal strength as a function of temperature between 5 and 120 K. The accuracy of the determination of temperature is within 1 K. Good agreement with a Curie law is obtained over the whole temperature range. This result is slightly different from that reported by Brodsky and Title[32] on a-Si prepared by glow discharge decomposition of silane gas: they find a Curie-Weiss $1/(T+\Theta)$ law where $\Theta = 1.2$ K. Although this is at the limit of our experimental accuracy, Θ appears to be negligible in our experiment. Fritzsche and Hudgens[54] found by bulk susceptibility measurements a Curie-Weiss law where $\Theta \simeq 5$ K dependent on annealing and indication of antiferromagnetic ordering below 10 K. On a-Ge Arizumi *et al.*[40] found a deviation at high temperature. The difference in results may originate in the noncontaminated nature of our films.

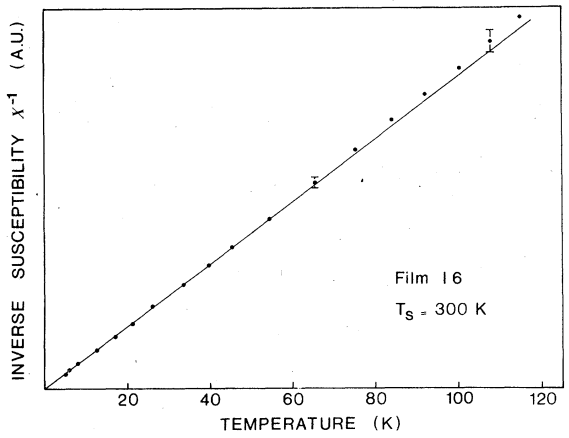

FIG. 16. Inverse of spin susceptibility versus temperature of a RT substrate deposited film. A good agreement with a Curie law is observed. Accuracy of the determination of temperature is about 1 K at temperatures of the order of 5 and 2 K at temperatures of the order of 100 K.

VI. DISCUSSION OF SPINS MODELS AND RELATION TO OTHER PROPERTIES

We will now discuss two main points which concern first, the distribution of the structural defects which give rise to the ESR signal. The two extreme cases are individual spins evenly distributed throughout the material and clusters of spins. The possible association of spins with voids is considered. Second, the characteristics of the paramagnetic electronic states which are seen by ESR and a possible connection of these states with other properties.

The idea of isolated spins is considered within the context of continuous-random-network models (CRN). In a CRN such as the Polk model, all covalent bonds are satisfied by allowing some distortions of the elementary tetrahedrons. Alternatively, one can build a cluster which has all bonds satisfied except for a single dangling bond. In doing so, one may in fact release some of the distortion energy that existed in the continuous structures. One can also consider the possible existence of isolated spins lying at special positions on the internal surfaces of voids.

The idea of clusters of spins takes its origin in radiation damage results and also with the different consideration of internal surfaces of voids. The ESR of damaged crystalline silicon can present features similar to a-Si. Many different defects, generally complicated, are created by radiation and depend on dose, energy and nature of the radiation. When crystalline silicon is damaged, for instance by implantation, complexes are created with a large number of dangling bonds. These have in general anisotropic ESR characteristics, but one could envisage a sufficiently large complex with interactions among the spins leading to a Lorentzian isotropic line. A limiting case of this would be the system of dangling bonds at the surface of a macroscopic void. This idea was first proposed because of Haneman's measurements of ESR of the [111] cleaved surface of crystalline silicon and crushed samples.[36,56] Haneman reported an ESR signal of g value 2.0055 and a signal strength proportional to the area of the cleaved surface. These results are now in doubt since Kaplan *et al.*[55] reported new experiments on the [111] cleaved surface of silicon which show no paramagnetic signal from the surface. Lemke and Haneman[57] subsequently confirmed that the surface signal, if it exists, is extremely small ($< 10^{-2}$ spins per surface atom). However even if no signal exists in the case of a crystal surface because for example of pairing of dangling bonds, a surface signal may exist in the case of amorphous void surfaces because the lack of symmetry may prevent a complete pairing occuring. If such a signal exists, one must expect a signal intensity roughly proportional to the total area of internal surfaces.

A. Nature of spins

To try to decide between isolated or clustered spins models, we do not use experimental data obtained on possibly contaminated films, i.e., we exclude results obtained on very thin films. We also do not consider annealed films where a different process for spin elimination seems to be involved. Two main results guide the discussion: the temperature dependence of the linewidth of films with different spin densities and the magnetic susceptibility. We have previously considered two terms in ΔH, ΔH_0, and ΔH_1. The analysis of ΔH_0 may give information about the nature of spins, as it can reveal the kind of interactions between spins. The important effect determining the temperature independent linewidth are (a) dipolar interactions, (b) g-factor anisotropy, and (c) exchange interactions.

Dipolar interactions and g-factor anisotropy are responsible for the basic linewidth. Exchange can reduce the value of linewidth due to the first two interactions.

It is possible to calculate the linewidth due to the dipolar interaction of a system of evenly distributed individual spins, and an order-of-magnitude estimate of the g-factor anisotropy can be obtained by comparison to the g-factor anisotropy of defects of implanted crystalline silicon.

We consider here a system of individual spins with negligible exchange interactions. The statistical theory of the dipolar interaction for a random spin distribution yields a line of Lorentzian character. (It is often written that dipolar interaction lead to a Gaussian line. Actually for randomly distributed spins the line is Lorentzian with a cutoff far in the wings.)

The temperature-independent Lorentzian linewidth is proportional to the spin density N_S and is given by[58]

$$\Delta H_D = (2\pi/3\sqrt{3})\gamma^2\hbar N_S \simeq 3,8\gamma^2\hbar N_S,$$

where ΔH_D is expressed in gauss, N_S in cm^{-3}, and γ is the gyromagnetic ratio. If we calculate ΔH_D for RT deposited samples ($N_S = 0.7 \times 10^{20}$ cm^{-3}) we obtain $\Delta H_D \simeq 5$ G which is in good agreement with the experimental value of ΔH_0. For the series of samples represented in Fig. 15, the proportionality of ΔH_0 to N_S is not strictly observed; for example between samples 0 and 1 there is a factor of about 2 between spin densities and only a factor of $\simeq 1.6$ for the corresponding ΔH_0. This implies that the dipolar interaction is not the only contribution to the linewidth.

Defects produced by implantation of crystalline

silicon have a g factor anisotropy. The g tensor of single-dangling-bond defects is generally axial with $g_{\parallel} - g_0 \sim 0$ and $g_{\perp} - g_0$ in the range 5×10^{-3}–10×10^{-3} (Ref. 59) (g_0 is the free-electron g value). Because of the random spin orientation, a-Si should have a spread of resonance fields which inhomogeneously broadens the line. If we assume that the observed g-value of 2.0055 is an average of such g tensors, we obtain $g_{\perp} - g_0 = 4.8 \times 10^{-3}$, this value corresponding to a spread of resonance fields of $\Delta H_g = 7.5$ G. This contribution is also of the right order of magnitude. Contributions to the temperature independent part of the linewidth of dipolar interaction and g-factor anisotropy are not simply additive. Moreover the composite line cannot be obtained by convoluting the two line shapes; this is due to the spin flip terms in the dipolar Hamiltonian which give rise to a dynamical narrowing effect. This problem has not been treated theoretically to our knowledge. Experimentally we find an increase of the peak-to-peak linewidth with spin density while other authors report the inverse behavior on differently prepared samples.[47] All results can be reconciled by considering a general linewidth variation versus spin concentration of the form as plotted in Fig. 17. The value at nearly zero spin concentration has its origin in the spread of g values. The initial decrease comes from narrowing by spin-flip interactions while the subsequent increase at high concentrations is the normal dipolar behavior.

Experiments at low spin concentrations or large-g-factor anisotropy (e.g., as in a-Ge) will show a decrease of linewidth with increasing spin density. It is a matter of conjecture whether the narrowing can be produced by the spin-flip part of the dipolar interaction alone, or an additional exchangelike contribution is needed.

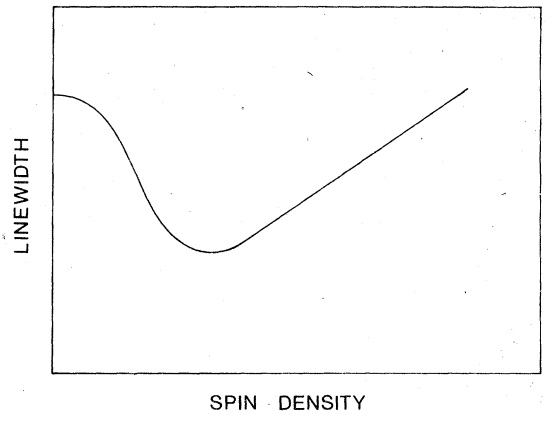

FIG. 17. Schematic representation of the linewidth vs spin density (linear scales).

To test this interpretation, we have made measurements at a frequency $\nu = 100$ GHz. At this frequency the g-factor anisotropy is the dominant term. In agreement with the above discussion, we find that the linewidth decreases with increasing spin concentration. These results will be published elsewhere.[60]

We note that a change of the dipolar-interaction value can produce a change of line shape. This explains qualitatively the data presented in Figs. 1(a)–1(d). A high value of dipolar interaction corresponding to RT deposited films leads to a nearly homogeneous spin system which gives a Lorentzian line shape and a nearly-well-defined longitudinal relaxation time T_1. As dipolar interaction is decreased (high-T_S deposited films), the spin system becomes inhomogeneous: the line shape deviates from a Lorentzian toward a Gaussian and a nearly defined T_1 is no longer deduced from saturation measurements.

Therefore we conclude that a model of evenly distributed individual spins is consistent with the linewidth behavior without the necessity of including exchange which may be negligible in this case.

We now examine a model of clusters of spins. We consider the extreme case where in each cluster, spins are separated by distances of the order of 4 Å which is the second-nearest-neighbor distance in silicon. In this case we expect a strong dipolar interaction between spins giving rise to a broad multiplet structure. This broad structure is going to be reduced by strong exchange interactions. As we have no precise knowledge of the cluster and the magnitude of exchange interactions it is not possible to calculate the resulting apparent linewidth. A test of the model follows from the behavior of the ESR susceptibility. If large exchange interactions exist the susceptibility must show a deviation from a simple Curie law at temperature $T \sim J/K$, where J is the exchange energy. The experimental error of the determination of the temperature being 1 K, we obtain an upper limit for the exchange energy J of 0.1 meV. From this value, we conclude that there is no evidence for strong exchange interactions. This limit is to be compared with the results of other authors who studied a-Si prepared by sputtering or glow discharge decomposition of silane. In contrast to the results of Brodsky and Title,[32] Fritzsche and Hudgens[54] observe a spin ordering in a-Si produced by decomposition of silane near 10 K. Brodsky and Title see a Curie-Weiss-like Θ of the order of 1 K which is not in disagreement with our results. Our measurements do not exclude the possibility of a fraction of small clusters. To clarify this point measurements at temperatures lower than liquid helium temperature are needed.

B. Location of spins

We looked for evidence connecting the spins to the internal surfaces of voids. By voids we mean defects larger than atomic size. Di-, tri-, tetra-, and pentavacancies are examples of atomic size defects. One such evidence would be a proportionality of the spin density to the voids surface area as it was formerly proposed by some authors.

We have tested this hypothesis in the angle evaporation experiment. The curve of Fig. 12 shows that in the absence of contamination spin density is independent of angle within experimental error. On the other hand, there is evidence that the void structure does change with angle: the decrease of spin density with air exposure for the 60° film indicates a large enhancement of porosity. As it seems unlikely that such a change in porosity is not accompanied by a large change in shape and internal surfaces area of voids, we think that we can exclude a simple proportionality relationship between ESR signal intensity and internal surfaces area of voids. We do not exclude that a fraction of spins is bound to voids. Air exposure effects which always lower the spin density seem to indicate that spins lie on internal surfaces of voids and can be eliminated by direct chemical bonding with a contaminant. However several other processes are possible such as a displacement of the Fermi level modifying the spin population.

C. Spins and other properties

We recall that the saturation behavior was found to depend very strongly on preparation conditions in contrast to other properties such as spin density or low-temperature linewidth. It is tempting as was done by others[31,41] to relate ESR saturation to conductivity which is another property varying strongly with preparation conditions: in our films the room temperature dc conductivity is found to vary by three orders of magnitude depending on substrate temperature. A possible model implying this relation is that of a basic hopping mechanism involving two dangling bonds:

$$D_0 + D_0 \rightarrow D_+ + D_-,$$

where D_0 are neutral paramagnetic dangling bonds and D_+, D_- are charged states of the same bonds. This mechanism totally relaxes spin energy because of the strong interactions between the two spins on the D_- bond.

In this model T_1 is simply the average time between hops τ_H and the relation to hopping conductivity is apparent. This average is site dependent and the inhomogeneous nature of the ESR line is thus understandable. It is a strong function of site concentration in agreement with observation.

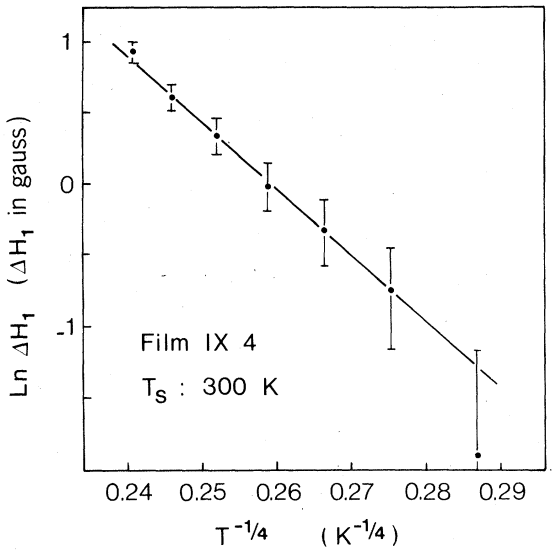

FIG. 18. Logarithm of the temperature-dependent part ΔH_1 of the linewidth fits at $T^{-1/4}$ law. Precision becomes poor when ΔH_1 tends towards zero.

Quantitative comparisons are however difficult since as we have noted, T_1 is in most cases not defined experimentally. In RT evaporated films, however, the line is almost homogeneous. One can derive in these films a value of $1/T_1$ from the temperature dependent contribution to the linewidth $\Delta H_1(T)$.

In the case of variable range hopping, the mean time between hops follows a $\ln(\tau_H) \alpha T^{-1/4}$ law. In Fig. 18 we have plotted the logarithm of ΔH_1 as a function of $T^{-1/4}$ for a RT deposited film between 140 and 300 K. The difficulty of measuring precisely the low value of ΔH_1 prevent extension of the range. The fit to a straight line is good. Although this shows that the model is definitively not in contradiction with experiment, is does not of course provide much additional weight for it since agreement obtained over limited ranges is not significant.

VII. CONCLUSION

Let us summarize the main results obtained in this work. The study of uncontaminated evaporated films has demonstrated that the deposition parameter governing the spin density is the substrate temperature. The variation of spin density obtained between $T_S = 300$ K and $T_S = 500$ K is about a factor of 2 so that spin density is almost an intrinsic constant of the evaporated material. This result is in sharp contrast with previous reports probably because their films were not contamination free.

The film porosity has been studied through the effect of air exposure on the spin characteristics.

RT deposited films are porous especially if evaporated at an angle. Films deposited at high temperature and normal incidence appear to be nonporous.

The nature of the spins has been investigated by studying the temperature dependence of the ESR intensity, linewidth, and saturation behavior.

A model of isolated dangling bonds is in agreement with our observations. No particular evidence for spin clusters is found, although the possibility that a fraction of the spins is in small clusters is not excluded. Study of ESR of films evaporated at an angle does not support any direct connection of spins to voids.

Finally an observed correlation between ESR saturation and conductivity is, to first approximation, consistent with a simple model involving hopping among dangling-bond sites.

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