Published in Journal of Applied Physics 80, issue 9, 4971-4975, 1996
which should be used for any reference to this work

Hydrogen in amorphous and microcrystalline silicon films prepared by hydrogen dilution

U. Kroll,[a] J. Meier, and A. Shah
Université de Neuchâtel, Institut de Microtechnique, rue A.-L. Breguet 2, 2000 Neuchâtel, Switzerland
S. Mikhailov and J. Weber
Université de Neuchâtel, Institut de Physique, rue A.-L. Breguet 1, 2000 Neuchâtel, Switzerland

Hydrogen incorporation in silicon layers prepared by plasma-enhanced chemical-vapor deposition using silane dilution by hydrogen has been studied by infrared spectroscopy (IR) and elastic recoil detection analysis (ERDA). The large range of silane dilution investigated can be divided into an amorphous and a microcrystalline zone. These two zones are separated by a narrow transition zone at a dilution level of 7.5%; here, the structure of the material cannot be clearly identified. The films in/near the amorphous/microcrystalline transition zone show a considerably enhanced hydrogen incorporation. Moreover, comparison of IR and ERDA and film stress measurements suggests that these layers contain a substantial amount of molecular hydrogen probably trapped in microvoids. In this particular case the determination of the total H content by IR spectroscopy leads to substantial errors. At silane concentrations below 6%, the hydrogen content decreases sharply and the material becomes progressively microcrystalline. The features observed in the IR-absorption modes can be clearly assigned to mono- and/or dihydride bonds on (100) and (111) surfaces in silicon crystallites. The measurements presented here constitute a further indication for the validity of the proportionality constant of Shanks *et al.* [Phys. Status Solidi B **110**, 43 (1980)], generally used to estimate the hydrogen content in ''conventional'' amorphous silicon films from IR spectroscopy; additionally, they indicate that this proportionality constant is also valid for the microcrystalline samples.

I. INTRODUCTION

The usual method for depositing hydrogenated amorphous silicon (*a*-Si:H) is by plasma-enhanced chemical-vapor deposition (PECVD) at low temperatures mostly from pure silane. Recently, the use of strong dilution of silane by hydrogen has attracted special attention for the fabrication of *a*-Si:H solar cells, because such cells show a reduced light-induced degradation.[1,2] Increasing the dilution of the silane by hydrogen even further leads to a morphological transition of the material into hydrogenated microcrystalline silicon (μc-Si:H). The latter material has also recently acquired a considerable interest as a photovoltaically active material.[3] Whereas the solar cells prepared in both regimes have already been studied in detail, it is surprising that much less is known about the layers themselves and their structural properties.

The structure of the material is particularly affected by the hydrogen incorporated and by its bonding configuration; both these factors act macroscopically on the internal mechanical stress. Furthermore, hydrogen certainly plays an additional crucial role by passivating the dangling bonds and, thus, improving the electrical and optical properties.

Hence, the studies mentioned above motivated us to investigate the hydrogen incorporated in the amorphous/microcrystalline silicon films deposited by hydrogen dilution and to determine the link between hydrogen incorporation and internal film stress. The material deposited in this study covered the large range from totally amorphous phase to completely microcrystalline phase passing over the transition region.

Quantitative analysis of H content was performed by infrared (IR), absorption spectroscopy and by elastic recoil detection analysis (ERDA). IR and ERDA must be considered as two independent methods. Generally, IR spectroscopy is used to estimate the hydrogen content in the layers, if the proportionality constant is known. This calibration constant correlates the strength of the IR-absorption bands due to the Si-H vibrations with the hydrogen content. It has been found for *a*-Si:H material[4] that the calibration constant of the integrated strength of the rocking–wagging–rolling vibrations around 640 cm^{-1} is independent of hydrogen content and of sample preparation. However, it is not evident that the proportionality constant formerly found still remains valid when the *a*-Si:H network is replaced by the hydrogenated microcrystalline silicon material as is the case in our study.

In contrast to IR spectroscopy, ERDA is an absolute method that determines the absolute total hydrogen content. Therefore, a comparison of the hydrogen contents determined by IR spectroscopy and by ERDA will allow us to verify if the proportionality constant has to be modified in the cases of hydrogenated microcrystalline silicon layers and of *a*-Si:H layers prepared from silane dilution by hydrogen.

II. EXPERIMENTAL DETAILS

The films were deposited in a capacitively coupled parallel-plate reactor using a plasma excitation frequency of 70 MHz instead of the standard industrial frequency of 13.56 MHz. Using the very-high-frequency (VHF) (70 MHz)

---

[a] Electronic mail. ulrich.kroll@imt.unine.ch

PECVD technique, an increased deposition rate as compared to 13.56 MHz is observed. Details are published elsewhere.[5] The silane concentration was varied from 100% to 1.25% by adapting the rations of the silane and hydrogen flows while keeping the total feed gas constant at 50 sccm; hence, the indicated silane dilution levels are the silane gas concentration of the fresh feed gas flowing into the reactor. Due to a different pumping speed of the process pump for hydrogen and silane, the absolute silane concentration in the reactor may slightly differ, but this does not affect the basis of our conclusions and interpretations in the following, since all layers were deposited using the same deposition system.

The depositions were performed at a pressure of 0.4 mbar, a HF-power input of 7 W, and a substrate temperature of 225 °C, as used by our group for the deposition of our ''standard'' microcrystalline silicon material, as incorporated in our *p-i-n* solar cells.[3] The HF power input is measured with a directional power meter in the 50 Ω line just before the matching network. Under these conditions, 1.5–2-μm-thick films were grown on Corning 7059 glass and on double-side-polished ⟨100⟩ Si wafers. Special care was taken to measure the film thicknesses with a surface profiler (Alpha Step 200 from Tencor Instruments) close to the area where the characterization experiments were performed. It has to be noted that a precise thickness measurement together with the use of thick samples enhance the accuracy of subsequent film characterization.

The total stress in the films was determined from the curvature of the Si wafer after deposition, measured with a surface stylus profiler. The total stress, which is the sum of intrinsic and extrinsic stress, was calculated using the equation and the constants given in Ref. 6. However, since the thermal expansion coefficients of the wafer and of the *a*-Si:H films are almost equal [$1.5–4\times10^{-6}$/K for *a*-Si:H (Ref. 7) and $2.6–3.8\times10^{-6}$/K for *c*-Si (Ref. 8)], the external stress created by thermal mismatch can be neglected. Thus, since no additional external force was applied, the determined stress essentially represents the intrinsic stress of the deposited films.

The IR-absorption measurements between 4000 and 400 cm^{-1} wave numbers were performed with a Perkin–Elmer Fourier transform IR (FTIR) spectrometer 1720 X on films deposited on ⟨100⟩ Si wafers. From the IR transmission spectra referenced to a plain Si wafer, the absorption coefficient was calculated according to the procedure described in the literature.[9,10] Special care was taken to ensure that the substrate and the reference wafers were from an identical batch to match them perfectly and avoid, thus, a contribution from the substrate *c*-Si phonon mode at 615 cm^{-1}. The hydrogen content C_H was obtained by numerical integration of the Si–H rocking–wagging mode[4,10] at 640 cm^{-1}. The complete procedure[4,9,10] can be expressed by the following equations:

$$C_H(\text{at. \%}) = \frac{A_w}{N_{Si}} \int_{\nu_{r/w}} \frac{\alpha(\nu)}{\nu}\, d\nu \approx \frac{A_w}{N_{Si}} \sum_{\nu_{r/w}} \frac{\alpha(\nu)}{\nu}\, \Delta\nu, \tag{1}$$

where $\alpha(\nu)$ is the absorption coefficient of the film at the wave number ν, $\nu_{r/w}$ stands for the rocking–wagging bands around 640 cm^{-1}, $A_w = 1.6\times10^{19}\ \mathrm{cm}^{-2}$ is the proportionality constant,[4] and $N_{Si} = 5\times10^{22}\ \mathrm{cm}^{-3}$ is the atomic density of pure silicon. It has to be noted that depending on the amount of hydrogen incorporated, the ''true'' atomic density of the amorphous silicon slightly augments; according to Beyer[11] the atomic density increases to values of $5.8\times10^{22}\ \mathrm{cm}^{-3}$ for *a*-Si:H layers containing hydrogen of around 20 at. %. Therefore, both the density variations as well as the global accuracy of the method limit here the accuracy of our results to about ±15% of the hydrogen content.

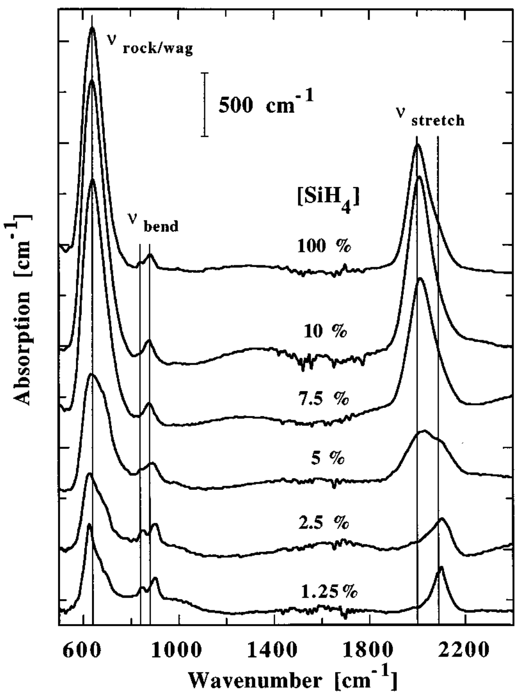

FIG. 1. IR-absorption spectra of layers prepared at different silane dilution levels as indicated in the figure; the spectra are shifted vertically for clarity.

The ERDA method consists in measuring the energy spectrum of protons (i.e., the hydrogen atoms) which have been elastically hit by incident alpha particles produced by a Van de Graaff accelerator and which recoil in a forward direction. The proton energy spectrum is a function of the hydrogen concentration profile of the sample to be investigated and of the alpha-beam intensity which is obtained from the Si signal measured simultaneously by Rutherford backscattering spectroscopy (RBS).[12] The experimental conditions of the measurements were: the incident angle of the α particles was 76.5°; the angles of detection were 20° for ERDA and 150° for RBS. Under these conditions the maximum detection depth under the film surface for hydrogen is approximately 0.8 μm and the overall accuracy of the hydrogen content is here around ±10%.

III. RESULTS AND DISCUSSION

Figure 1 shows the absorption obtained from the IR-transmission measurements of samples prepared at different silane dilution levels. The dilution levels indicated in the figure represent the silane gas concentrations of the fresh feed gas flowing into the reactor. The thin vertical lines in the graph indicate the peak positions of the different absorption modes for pure hydrogenated amorphous silicon material[9,13] at 640, 840, 880, 2000, and 2090 cm^{-1}. The IR modes of the samples deposited from pure silane down to silane concentrations of 7.5% retain the typical fingerprint pattern, pertaining to a bonding structure of hydrogenated amorphous silicon. However, for concentrations less than 7.5% the typical amorphous modes gradually disappear and parallel to this new, much narrower peaks arise mainly around 626, 900, and 2101 cm^{-1} (see Fig. 1). Generally, at these low silane concentrations, as commonly used for the preparation of μc-Si:H material, it can be observed that there is a narrowing of the absorption bands, and that at the same time the vibration frequencies of the rocking–wagging modes are shifted to lower frequencies and those of the stretching modes to higher frequencies. The latter observations are a clear indication for changes in the hydrogen bonding nature and in the bonding environment. By comparison with the results presented in Refs. 14–17, all these vibration modes (i.e. the rocking–wagging, bending, and particularly the different stretching modes around 2100 cm^{-1}) can be clearly assigned to mono- and/or dihydride bonds on (100) and (111) surfaces in silicon crystallites.

Therefore, we conclude that in this dilution range, apart from a certain amount of amorphous phase still present, formation of microcrystallites occurs and the hydrogen is preferentially bonded at the surfaces of the microcrystalline grains. Indeed, independent of these IR-absorption measurements, other characterization techniques such as x-ray diffraction and optical-absorption measurements in the visible range also confirm that at dilution levels below a feed gas silane concentration of 7.5% the films obtained start to become microcrystalline:[18] The continuously occurring modifications of the IR spectra within the microcrystalline dilution range suggest that the material deposited here consists of a crystalline and of an amorphous phase, in a variable composition; this composition depends on the exact value of the dilution. Hence, by looking at the H bonding by IR-absorption spectroscopy we are able to detect even small gradual structural and compositional differences for layers deposited at different silane concentrations in the microcrystalline regime.

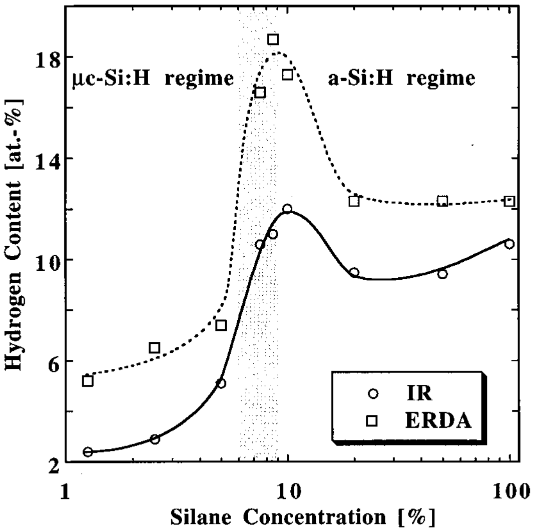

FIG. 2. Hydrogen content of the films determined by IR spectroscopy and by ERDA as a function of the silane concentration; the gray highlighted area represents the amorphous/microcrystalline transition zone. The lines are merely for guiding the eye.

Figure 2 shows the total hydrogen content of the layers determined by IR spectroscopy and ERDA as a function of silane dilution during the deposition. With respect to the results discussed above, we fundamentally divided the total dilution range into a first zone above a silane concentration of 9% and up to pure silane; in this zone the deposited samples have a completely amorphous structure; secondly we distinguish a zone below a silane concentration of 6% where clearly microcrystalline material has been deposited. These two zones are separated by a narrow transition zone which is highlighted in gray in the figure. In this transition zone the structure of the material is not clearly identifiable. In our case we consider the structure as clearly identified if independently, IR spectroscopy, x-ray-diffraction measurements, and optical-absorption measurements all lead to the identical conclusion.

For the determination of the total bonded hydrogen content by IR spectroscopy the rocking–wagging vibration mode around 640 cm^{-1} was used, since in the case of the a-Si:H structure the oscillator strength is independent of the preparation conditions and of the H content[4] for this mode. However, two basic difficulties can arise which may strongly alter the proportionality constant between the H content and the integrated absorption when structural changes occur:

(1) The bonds in solids which see the local electromagnetic field may be considerably influenced by the different microscopic structure; and
(2) the oscillator strength of a given mode of the Si—H bond can be strongly affected by the changed molecular environment.

The total hydrogen content has been additionally measured by ERDA, the latter being a direct method to determine the total amount of bonded and nonbonded hydrogen in the films. The H content as a function of the dilution ratio determined by both methods (Fig. 2) shows an identical overall tendency and no significant systematic difference in the trends is apparent. Note that a general overall shift in the absolute hydrogen contents of the two independent methods arises, due to inaccuracies in the calibration constants. On the other hand, it is reasonable that ERDA determines a higher H content than the IR measurements, because IR spectroscopy detects only the bonded hydrogen, whereas ERDA is sensitive to all the hydrogen. Hence, ERDA additionally detects the molecular hydrogen trapped in internal microvoids or microcavities present in the material. It has been shown, e.g., by calorimetrical experiments that the molecular hydrogen in a-Si:H layers can attain substantial amounts.[11,19]

Furthermore, both methods confirm that the hydrogen incorporation in the a-Si:H material prepared at dilution ratios close to or within the transition zone is considerably enhanced, as compared to films prepared from pure silane.

A further increasing dilution beyond the transition zone

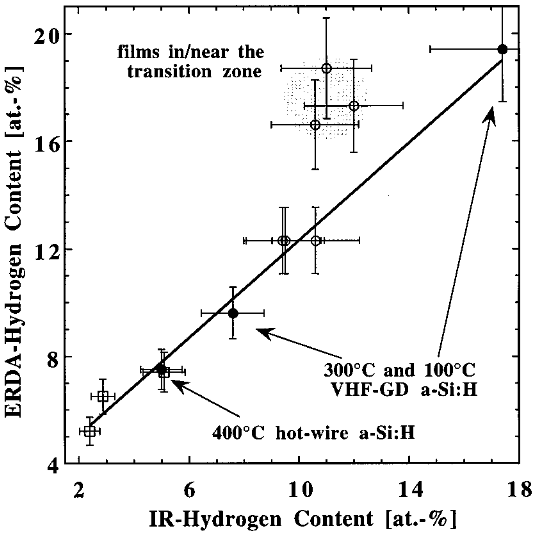

FIG. 3. Hydrogen content determined by ERDA plotted against the hydrogen content obtained by IR spectroscopy; the squares are samples prepared in the μc-Si:H regime having a clear microcrystalline character whereas the gray highlighted circle represents the films deposited in or very near to the amorphous/microcrystalline transition zone. Furthermore, conventional a-Si:H samples (black points) deposited in our laboratory from pure silane at different temperatures (100, 300, and 400 °C) and/or using the hot-wire technique are added, for the purposes of comparison. The straight line is fitted by hand.

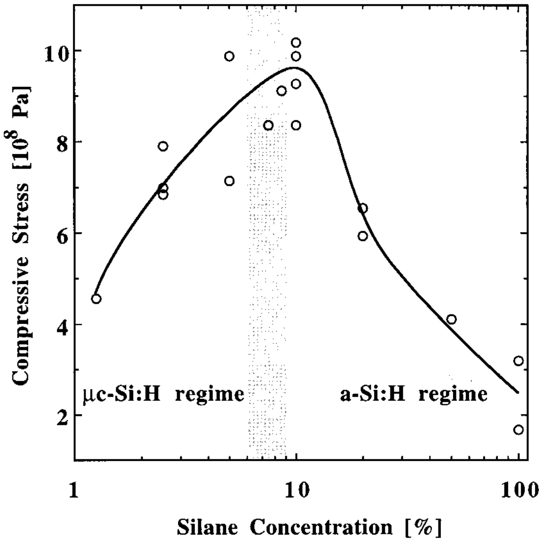

FIG. 4. Compressive film stress as a function of the silane concentration. The line is merely for guiding the eye.

leads to μc-Si:H growth together with a strong reduction of the hydrogen content even well under the contents of samples prepared in the amorphous regime. The values found here for the μc-Si:H are in agreement with former ERDA and hydrogen effusion measurements.[20]

In order to establish if there exists a proportionality constant between the integrated strength of the rocking–wagging vibration mode and the H content in the whole investigated dilution range we have plotted, in Fig. 3, the hydrogen content determined by ERDA against the H content obtained by IR spectroscopy for the same samples. Additionally for the purpose of comparison, we have plotted the data of three conventional a-Si:H films deposited from pure silane by the VHF PECVD and by the hot-wire technique at different substrate temperatures. The H contents of these conventional a-Si:H samples span over a large range similar to that of the H content of the layers prepared by hydrogen dilution.

Omitting the samples in/near the narrow transition zone (note: the transition zone represents only a very small part of the whole dilution range investigated), all other samples prepared by dilution lie, quite independently of the dilution level and of the structural properties, on a single straight line which coincides very well with the line found for the conventional a-Si:H layers. Since the slope of the straight line is close to 1, our measurements reconfirm the proportionality constant given by Shanks *et al.*[4] for conventional a-Si:H and moreover extend the validity of this proportionality constant, additionally, to μc-Si:H layers.

The only values off the straight line in Fig. 3 are due to the films deposited in/near the narrow transition zone (represented by a gray highlighted circle in the figure); it is caused from a extraordinary increased H content measured by ERDA as compared to IR measurements and indicates a higher incorporation of nonbonded hydrogen in the matrix. In particular, the increased difference between IR and ERDA in this region might suggest a higher amount of molecular hydrogen enclosed in microvoids. In accordance with this, a substantially increased amount of molecular hydrogen in the microvoids should microscopically increase the gas pressure in the microvoids for comparable structures, and, by this, increase the macroscopically observable stress. Indeed, as shown in Fig. 4, a substantially increased compressive stress has been found for layers in or near to the transition zone. Due to the high compressive stress, these layers have a very strong tendency to peel off from the substrate.

For the process of molecular hydrogen incorporation into the film we propose the following model: Caused by the plasma a certain amount of atomic hydrogen will be present at the film growth zone. Partially, this atomic hydrogen will penetrate into the subsurface growth zone by diffusion and reconstruct, there, the Si–Si network structure either by etching weak Si—Si bonds, or by saturating present dangling bonds, or, also, by reacting with clustered hydrogen.[21] The molecular hydrogen, thus formed, is now less able to diffuse than the atomic hydrogen; therefore, it is not volatile enough to reach the gas phase again before being buried by further deposition and hence being definitely trapped in the bulk material.

Assuming that more hydrogen present in the plasma also increases the concentration of molecular hydrogen at the growing surface, the simple image described above lets us basically understand the experimentally found observations that both the bonded as well as the molecular hydrogen in the still amorphous material increase by strong dilution. On the other hand, we have to concede that this model is very simplified and surely does not fully describe the actual, complex mechanism of hydrogen incorporation and growth kinetics.

IV. SUMMARY AND CONCLUSIONS

Silicon layers have been deposited using silane dilution by hydrogen over the large dilution range from 100% silane down to 1.25%. According to the structure of the material obtained, this large dilution range can be divided into two major zones separated by a narrow transition zone. A first major zone corresponds to amorphous material and covers the range from pure silane down to silane concentrations of about 9%. In this zone the layers deposited indeed have a fully amorphous structure. At silane concentrations below 6% the hydrogen content of the films decreases sharply as confirmed by ERDA and IR spectroscopy, and the material becomes microcrystalline as also recognizable in the IR spectra. It can be noted that IR-absorption spectroscopy detects even small, gradual differences in these layers. The observed modifications and features in the IR-absorption modes can be clearly assigned to mono- and/or dihydride bonds on (100) and (111) surfaces in silicon crystallites.

At silane concentrations between 6% and 9%, we observed a narrow transition zone; here, the structure of the layers deposited cannot be clearly identified. The films in/near the transition zone show a considerably enhanced hydrogen incorporation as compared to a-Si:H prepared from pure silane. Moreover, IR spectroscopy and ERDA suggest that in this transition zone a much higher amount of molecular hydrogen (probably trapped in microvoids) is incorporated in the layers. In the same dilution region the intrinsic compressive film stress reaches its maximum; this is consistent with our observation of a higher amount of molecular, nonbonded hydrogen being trapped in the material. However, the exact mechanism of hydrogen incorporation within this transition zone, and the detailed consequences of all this on film properties, is still poorly understood and requires further investigation.

Finally, our measurements indicate that the commonly used proportionality constant between the integrated absorption strength of the rocking–wagging vibration mode and the hydrogen content as given in Ref. 4 remains valid for the fully amorphous layers deposited at moderate dilution and is additionally applicable to the microcrystalline layers deposited at high dilution. Therefore, the usual evaluation method which is well established for conventional a-Si:H can be extended to estimate the hydrogen content in μc-Si:H material.

However, in the specific layers as deposited in/near the narrow transition zone, IR spectroscopy strongly underestimates the total hydrogen content due to the high amount of molecular, nonbonded hydrogen present here. Hence, high compressive film stress considered to be a potential sign for increased levels of molecular hydrogen reminds us to use IR spectroscopy with care for determination of total H content.

ACKNOWLEDGMENTS

We would like to thank Y. Ziegler for providing the hot-wire sample and S. Dubail for his technical assistance. The work was supported by the Swiss Federal Office of Energy (OFEN) under Contract No. EF-REN(93)032 and by the Swiss National Science Foundation under Contract No. 2000-041854.94.

[1] J. Yang, X. Xu, and S. Guha, Mater. Res. Soc. Symp. Proc. **336**, 687 (1994).

[2] R. Platz, D. Fischer, C. Hof, S. Dubail, U. Kroll, and A. Shah, to be presented at Mater. Res. Soc. Spring Meeting, San Francisco, 1996.

[3] J. Meier, R. Flückiger, H. Keppner, and A. Shah, Appl. Phys. Lett. **65**, 860 (1994).

[4] H. Shanks, C. J. Fang, L. Ley, M. Cardona, F. J. Demond, and S. Kalbitzer, Phys. Status Solidi B **110**, 43 (1980).

[5] A. Howling, J.-L. Dorier, Ch. Hollenstein, U. Kroll, and F. Finger, J. Vac. Sci. Technol. A **10**, 1080 (1992).

[6] M. Stutzmann, Appl. Phys. Lett. **47**, 21 (1985).

[7] T. Dragone, S. Wagner, and T. D. Moustakas, in Technical Digest of the 1st International Photovoltaic Science and Engineering Conference, 1984, p. 711.

[8] T. Soma and H.-M. Kagaya, *Properties of Silicon*, EMIS Datareviews Series No. 4 (Institution of Electrical Engineers, London, New York, 1988), p. 33.

[9] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

[10] A. A. Langford, M. L. Fleed, and M. H. Mahan, Sol. Cells **27**, 373 (1989).

[11] W. Beyer, in *Tetrahedrally Bonded Amorphous Semiconductors*, edited by D. Adler and H. Fritzsche (Plenum, New York, 1985), p. 129.

[12] X.-M. Tang, J. Weber, Y. Baer, and F. Finger, Solid State Commun. **74**, 171 (1990).

[13] G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).

[14] H. Wagner and W. Beyer, Solid State Commun. **48**, 587 (1983).

[15] Y. J. Chabal, E. E. Chaban, and S. B. Christman, J. Electron Spectrosc. Relat. Phenom. **29**, 35 (1983).

[16] Y. J. Chabal, Phys. Rev. Lett. **50**, 1850 (1983).

[17] T. Satoh and A. Hiraki, J. Appl. Phys. **24**, L491 (1985).

[18] J. Pohl (private communication).

[19] H. von Löhneyesen, H. J. Schink, and W. Beyer, Phys. Rev. Lett. **52**, 549 (1984).

[20] F. Finger, K. Prasad, S. Dubail, A. Shah, X.-M. Tang, J. Weber, and W. Beyer, Mater. Res. Soc. Symp. Proc. **219**, 383 (1991).

[21] R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge 1991), Sec. 2.3.4.