Selective low-power plasma decomposition of silane-methane mixtures for the preparation of methylated amorphous silicon

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(Received 26 February 1988; revised manuscript received 15 July 1988)

We report on a systematic study of the deposition and the physical properties of amorphous-silicon–carbon alloys produced by glow discharge from silane-methane mixtures. We define a "low-power" regime of preparation in which the chemistry of deposition is separated from the chemistry of the plasma. In this regime there is no primary decay of the methane, which then acts as a buffer gas. The carbon is incorporated in the solid only by reaction of the methane gas with the active species produced by the plasma decomposition of the silane. In this mode of preparation, we find the following. (1) The physical properties (in particular, the optical properties) are insensitive to the preparation conditions, depending mostly on the methane-to-silane ratio. (2) There is a smooth "chemical" incorporation of carbon in the amorphous silicon network, giving an alloy with good semiconducting properties. (3) The amount of carbon that can be incorporated is limited to less than 40 at. %, whereas in the high-power regime alloys can be produced with arbitrary [C]/[Si] proportions. (4) In the low-power regime the carbon is incorporated mostly in the form of methyl groups CH_3, so that the material produced in this condition should be labeled as "methylated amorphous silicon."

I. INTRODUCTION

The analysis of the semiconducting and optical properties of amorphous silicon has made large progress in the past few years. The conditions under which high-quality films can be prepared by glow-discharge deposition have been well identified. Consequently, device-grade material for solar-cell applications, prepared in different reactor types and laboratories, exhibits almost the same physical properties.

In the case of amorphous hydrogenated IV-IV alloys, this point of convergence has not yet been reached. The preparation of these materials is far more complex, since a variety of gas mixtures can be used in the depositions, and the chemical affinities of hydrogen to the elements in the alloys are in general very different. The most thoroughly studied alloy systems are a-$Si_{1-x}C_x$:H and a-$Si_{1-x}Ge_x$:H. Both the Si-C-H and the Si-Ge-H systems represent a wide variety of materials, with properties depending strongly on preparation conditions. While a-$Si_{1-x}Ge_x$:H films in general exhibit rather poor optoelectronic properties due to high disorder and heterogeneous texture, the electronic quality and disorder of a-$Si_{1-x}C_x$:H films, if prepared under suitable conditions, remain at a level comparable to that of pure a-Si:H,[1] in spite of a large variation of optical properties. In that respect, amorphous hydrogenated silicon-carbon alloys, besides their relevance to solar cell fabrication, represent an exemplary material for fundamental studies of an amorphous system with variable disorder.[2]

In a preliminary study[3] we have been able to detect a systematic difference between two groups of materials prepared from SiH_4+CH_4 mixtures: At high rf power density, films containing silicon and carbon in any proportion can be deposited,[4] whereas at low rf power density, low density-of-states material is obtained with a maximum carbon content of about 40% (all the concentrations in this article are given in at. %).

In the present paper, we present a systematic study of this "low-power regime" for the deposition of amorphous hydrogenated silicon-carbon films from SiH_4-CH_4 mixtures. We give a simple phenomenological definition of the low-power regime, and we develop a simple chemical model that can explain all the peculiar features of this regime, including the high electronic quality of the material and the insensitivity of its optical properties to a variation of deposition parameters. The existence of such a deposition regime, due to its inherent reproducibility, greatly simplifies the research and development in the field of a-$Si_{1-x}C_x$:H films.

II. EXPERIMENT

The capacitively coupled radio-frequency reactor used in the present work has been described earlier.[5] Films were deposited on glass plates clamped to the heated anode. Silane and methane flows were controlled by flowmeters. Central deposition parameters are substrate temperature 250 °C, pressure 40 mTorr, power density 0.06 W/cm^2, gas-flow rate 20 cm^3/min, interelectrodes distance 3.8 cm. Parameters outside of these values were chosen for complementary studies.

The films so obtained have been characterized by a wide range of techniques: optical spectroscopy,[5,6] photoelectron spectroscopy,[2] space-charge-limited current analysis,[7] photothermal deflection spectroscopy,[8] and different methods for chemical analysis as discussed in Sec. III C.

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III. RESULTS AND DISCUSSION

A. The low-power regime

The power threshold for the decomposition of methane CH_4 in a reactor is higher than that of silane SiH_4.[9,10] In the present work, we apply a power density which remains below that threshold, so that there is no primary decomposition of the methane by the plasma: this is our definition of the "low-power regime."

This is best illustrated in Fig. 1 where we have plotted the deposition rate of the films as a function of the concentration of the methane in the silane-methane mixtures. Several features of this curve are characteristic of the low-power regime.

(i) In this regime, the rate of direct decomposition of the methane is very small, so that the rate of deposition of carbon from a glow discharge in 100% methane is vanishingly small. A zero deposition rate of pure carbon can be used as a practical definition of the low-power regime.

(ii) A striking result seen in the figure is that the deposition rate for a constant rf power applied to the plasma is practically independent of the gas-phase composition over a wide range of concentrations. We can show that this is a direct consequence of our conditions of the nonprimary decomposition of CH_4 in the plasma. Since only the silane is decomposed, the deposition rate V is roughly proportional to the concentration of silane, $[SiH_4]$, and to the density of electrons, N_e, having enough energy to decompose the silane:

$$V \approx N_e[SiH_4] \; . \tag{1}$$

On the other hand, the tail of energetic electrons in the electron energy distribution is limited by inelastic collisions which, by the definition of the low-power regime, can only occur on silane molecules so that for a constant applied power to the plasma

$$N_e \approx 1/[SiH_4] \; . \tag{2}$$

Thus, this very simplified argument shows that the deposition rate is independent of the silane concentration. It applies to the partial pressure of silane mixed with methane, as well as to the total pressure, as long as the mean-free path remains short compared to the interelectrode distance. Of course the same argument would be valid for any buffer gas having only elastic collisions with the electrons of the plasma.[11] This is shown in Fig. 1 by the square point, where we have replaced a 50–50% mixture of silane methane by the same ratio of a silane-helium mixture: The deposition rate remains the same.

At the far end of the methane-rich side the deposition rate decreases, reaching eventually zero for pure methane. In this region, there is not enough silane gas to be decomposed in the plasma and the rate of deposition decreases. This "silane-starving" effect can be reduced by increasing the flow rates. This is demonstrated in Fig. 1 by the triangular points, obtained by increasing the flow rate of the silane-methane mixture by a factor of 4, increasing the pumping speed by the same factor so as to keep the total pressure constant. As expected, the rate of deposition increases for the points corresponding to the highest concentration of methane. In the limit of an infinite flow rate and pumping speed, we would expect an even sharper drop from a finite to a zero-deposition rate for pure methane. This constant value of the deposition rate with the silane-methane composition of the gas is characteristic of the "low-power regime" which corresponds, in our reactor, to power densities lower than 0.3 W/cm^2. For larger powers, one finds in general a deposition rate decreasing continuously as the methane concentration increases.[4]

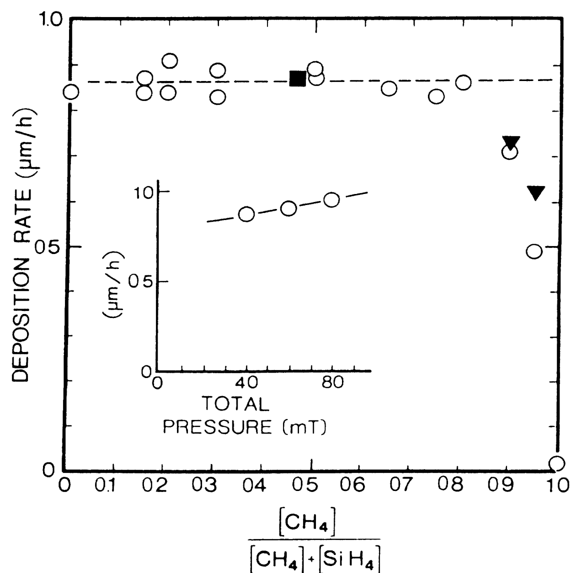

FIG. 1. Deposition rate as a function of gas-phase composition. ■: the methane is replaced by the same proportion of helium. ▼: the flow rates of the gases and the pumping speed have been multiplied by a factor of 4. Inset: Deposition rate as a function of the total pressure for pure silane. The deposition rate drops to zero for pure methane, which defines our "low-power" regime. In this regime, the deposition rates are fairly insensitive to the partial and total pressure of silane, except in the silane-starved region where the proportion of methane is very large (> 85%).

B. The "chemical" model of carbon incorporation

Since there is no primary decomposition of the methane in the low-power regime, the incorporation of carbon in the film can only result from a chemical reaction between the "species" (SiH, SiH_2, SiH_3, H, etc.) created by the plasma from the silane and the CH_4 molecules. This "chemical" model of carbon incorporation explains many of the properties of the material.

(i) In the conditions optimized for a-Si:H deposition, one might expect that the chemical incorporation of carbon would not perturb the formation of the random network too much. And indeed, it is found[12] that the density of states of the material remains that of pure a-Si:H even for a rather large incorporation of carbon. The good semiconducting properties of the low-power carbonated silicon explains the successful use of this materi-

al, both doped and undoped, as a front layer for solar cells.[13]

(ii) These films of $Si_{1-x}C_x$ obtained from SiH_4-CH_4 mixtures in the low-power regime show properties remarkably insensitive to the conditions of deposition: They depend almost exclusively on the methane-to-silane ratio. For example, the optical properties of the films are shown in Fig. 2. For the determination of the optical gap, we avoid the use of the conventional Tauc plot which requires an extrapolation subject to relatively large errors. Instead, we have plotted the energy E_{04} at which the absorption coefficient equals 10^4 cm^{-1}. The difference between E_{04} and the Tauc gap amounts to about 0.15 eV in our samples[12] and is not significant for the present discussion. In this figure n_0 is the value of the refractive index extrapolated to infinite wavelength.

As shown in Table I the values of E_{04} do not vary, within experimental errors, for a wide range of deposition parameters around the central conditions given in Sec. II.

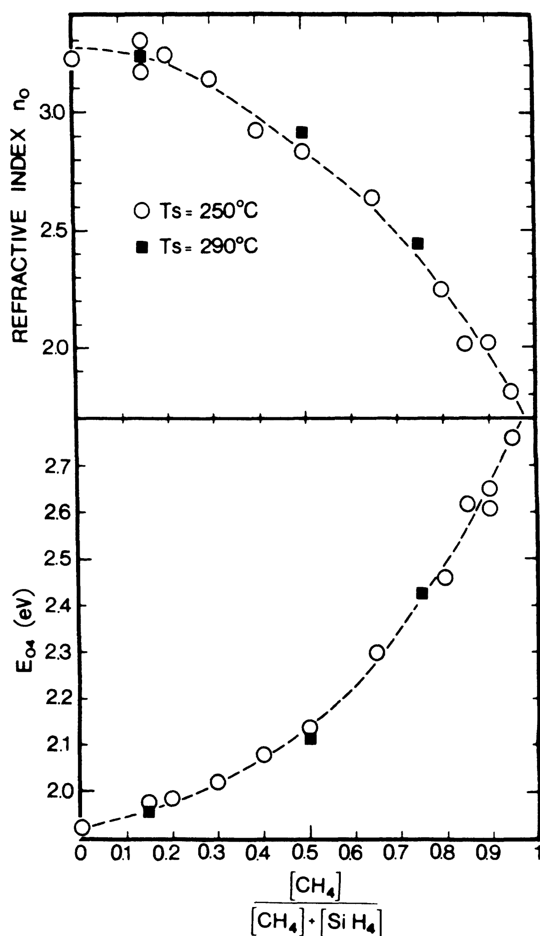

FIG. 2. The static refractive index n_0 and E_{04} (energy at which the absorption coefficient is 10^4 cm^{-1}) as a function of the gas composition in the low-power regime of deposition. We obtain practically "universal" curves, very insensitive to the preparation parameters: substrate temperature, total pressure, power density, flow rates, and geometry of the reactor.

TABLE I. Variations of E_{04} with the deposition parameters. The values of E_{04} are obtained for a methane concentration of 65%. The parameter being varied is indicated in the table, the other deposition parameters are those given in Sec. II. For the range of parameters shown in the table, the value of E_{04} is constant within the estimated measurement error of ±20 meV.

		E_{04} (eV)
Total pressure (mTorr)	30	2.289
	90	2.279
Power density (W/cm^2)	0.04	2.265
	0.25	2.280
Flow rate (cm^3/min)	16	2.276
	50	2.273
Interelectrode distance (cm)	2.7	2.301
	5.0	2.276

(1) Total pressure from 30 to 100 mTorr. The deposition rate also does not vary much with the total pressure (inset in Fig. 1) as expected from the discussion in Sec. III A.

(2) Total flow rate from 16 to 67 cm^3/min. However, for a gas mixture with more than 85% of CH_4, we are in the silane-deficient region (Fig. 1) and both the deposition rate and the optical properties become dependent upon the flow rates.

(3) Interelectrodes distance from 2.7 to 5 cm. Beyond 5 cm, the film thickness decreases from the center to the edges and the sample is not homogeneous enough for optical studies. A remarkable result, illustrating the chemical model of carbon incorporation, is that the optical properties seem to be quite reactor independent: Curves identical to that of Fig. 2 have been obtained with a reactor of a very different size and type.[14]

(4) Power density from 0.04 to 0.3 W/cm^2. The optical properties of the samples are insensitive to the rf power (i.e., to the deposition rate) as long as the low-power re-

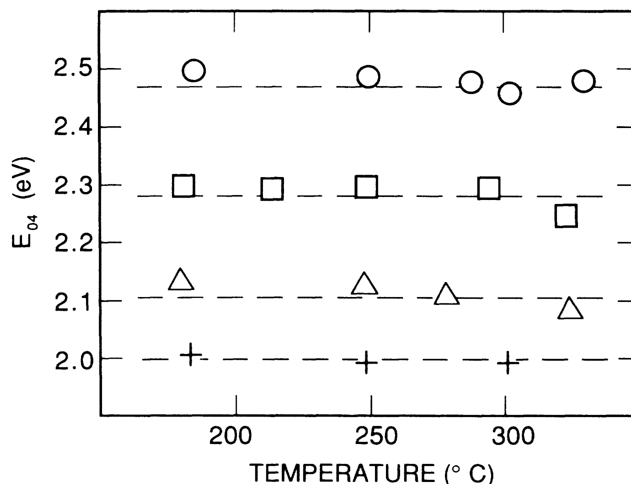

FIG. 3. E_{04} as a function of the deposition temperature, for different concentrations of methane in the gas mixture: ○, 80%; □, 65%; △, 50%; and +, 20%.

gime is maintained. This is in contrast with the high-power deposition (above 0.3 W/cm^2), in which the concentration of carbon increases strongly with power.[4]

(5) The variation of E_{04} with the deposition temperature is shown in Fig. 3. The gap is practically constant from 180 °C to 320 °C, and start decreasing only above 340 °C.

We remark that the quantities directly observable concerning the gases are usually the flow rates. Now, in order to have "universal curves" as in Fig. 2, it is necessary to express the results as a function of the partial pressures of the silane and methane. Depending upon the type of pumping (molecular or viscous regime) different corrections must be applied to obtain the partial pressures from the flow rates. In particular, intermediate cases are difficult and require a careful study.

The chemical model of carbon incorporation in the low-power regime can explain qualitatively why the properties of the films depend mainly on the methane-to-silane ratio. In this regime the active "species" result only from the decomposition of the silane. They will react with the silane and methane molecules to produce deposition precursors that will depend mostly upon the methane-to-silane proportion. Two conditions are required for this simplified situation.

(1) The concentration of active species has to be small compared to the concentrations of the stable gases, silane, and methane. This excludes the silane-deficient region, when the concentration of silane is too small. As we have seen before, this region, depending somewhat on the flow rates (see Fig. 1), corresponds to concentrations of methane larger than 85–90 %.

(2) The nature of the active species should not vary too much with the plasma conditions, which is a quite reasonable assumption in the rather small range of power used in the present conditions. In contrast, this condition would clearly be violated in the "high-power" regime where active species, resulting both from the decomposition of the silane and the methane, would be produced in a proportion that is expected to be very power dependent and more generally to depend upon the nature of the glow-discharge plasma. In this high-power regime, therefore, the nature of the $Si_{1-x}C_x$ films will not depend simply upon the gas ratio, but also significantly upon the deposition conditions.[4]

C. Carbon incorporation in the solid: Results and limitations

The determination of the absolute concentrations of the different elements in an amorphous silicon alloy is not a trivial problem. Several methods have been used: nuclear techniques, infrared spectroscopy, soft x rays, Auger spectroscopy, microprobe analysis, etc. Most of these methods cannot give absolute values of the concentration in the films and require in general a reference film of alloy. This is illustrated in Fig. 4 where we have collected a series of absolute carbon concentration measurements on our films by different methods: Rutherford backscattering,[4] microprobe analysis, x-ray photoelectron spectroscopy,[15] direct chemical analysis, and Auger spec-

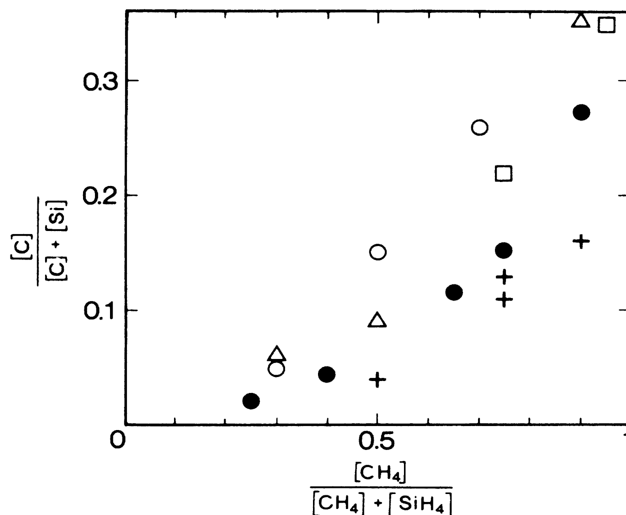

FIG. 4. Carbon concentration in the solid, as a function of the gas-phase composition, obtained by different analytical methods. ○, Rutherford backscattering; ●, chemical analysis; □, x-ray photoelectron spectroscopy; +, Auger spectroscopy; △, microprobe analysis. The points obtained by chemical analysis are considered as the most reliable for absolute measurements and have been reported on Fig. 5.

troscopy. The latter is obtained from a comparison of the 272-eV carbon line and the 92-eV silicon line with the proper sensitivity corrections.[16] The spread of the absolute concentrations is quite large, although the relative measurements for each method is probably more reliable. Nuclear magnetic resonance gives a precise measure of the concentration of hydrogen but is difficult to apply to silicon and carbon. Finally, the direct chemical analysis[17] of the absolute concentrations of the elements Si, C, H in the films seems to provide the most reliable method, limited to a relative precision for each element of ±2%. Since this concentrations of the elements are determined independently, a good check of the analysis is to verify that the sum of the measured concentrations is close to 1. For the five alloys measured this was the case to within ±4%. The main difficulty of the method is to require a rather large amount of material, of the order of 0.1 g, corresponding to long deposition times.

Finally, the atomic concentration of carbon incorporated in the films measured by chemical analysis is plotted as a function of the methane concentration in Fig. 5. Since this analysis is a rather tedious process, we have limited the measurements to material deposited with the standard conditions of Sec. II except for one sample deposited at higher power, but still within the low-power regime. We infer the insensitivity of the carbon concentration with the deposition conditions from the optical results discussed in Sec. III B. As can be seen in the figure, in the low-power regime the carbon incorporation is surprisingly low; even with 90% of methane, the carbon concentration in the film remains below 30%. In almost pure methane, which can only be an extrapolation since for zero silane concentration the deposition rate drops to zero, we would still obtain films containing some

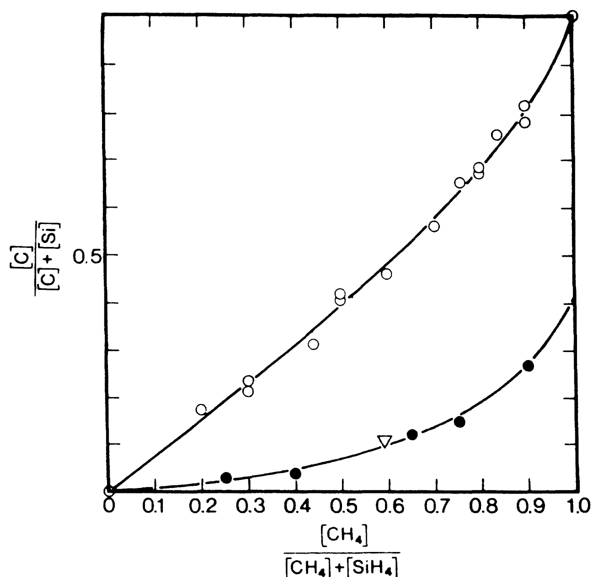

FIG. 5. Carbon incorporation in the films as a function of the gas-phase composition. ○, at high power (Ref. 4) carbon can be incorporated in the solid in all proportions. ●, in the low-power regime of deposition (present work, standard conditions given in Sec. II), the carbon incorporation remains below 40%. △, sample deposited at higher power (0.25 W/cm^2), but still in the low-power regime. The solid line is given by Eq. (5) (see text).

60% of silicon. This is a very direct illustration of the chemical model of carbon incorporation in this material. It is possible to obtain from these measurements semiquantitative information on the reactivity between the active species created by the plasma and the stable gases, methane and silane. We make a very simple model based on empirical rate equations:

$$[C]=\alpha=\frac{[CH_4]}{[SiH_4]+[CH_4]} , \tag{3}$$

$$[Si]=\beta\frac{[SiH_4]}{[SiH_4]+[CH_4]}+\gamma . \tag{4}$$

In these equations, the square brackets indicate the concentrations in the solid and the gases. The quantities α and β are proportional to the respective reaction probabilities of the active species with the methane and silane. γ indicates the possibility of direct deposition of silicon in the film from the radicals created by the decomposition of the silane. There is no corresponding term in Eq. (3) since in the low-power regime there is no direct decomposition of the methane. In this model, we try to include in a single parameter (α, β, or γ) not only the gas-reaction probabilities, but also surface effects, sticking coefficients, etc. Whatever the limitations of this extremely simplified and intuitive formulation, we believe that it contains most of the physical features of the actual deposition processes in the low-power regime. From these two equations, we obtain the equation of the concentrations in the solid as a function of the concentrations in the gases:

$$s=\frac{\alpha g}{(\beta+\gamma)+(\alpha-\beta)g} , \tag{5}$$

where

$$s=\frac{[C]}{[Si]+[C]} , \tag{6}$$

$$g=\frac{[CH_4]}{[SiH_4]+[CH_4]} . \tag{7}$$

We get a good fit with the experimental results (solid curve in Fig. 5) by setting $\alpha/\beta=0.10$ and $\gamma/\beta=0.14$. The fact that the active species of the plasma react about 10 times less with methane than with silane, expressed by the low value of $\alpha/\beta=0.10$, is quite reasonable if one considers the chemical stability of the two gases.

In the high-power regime,[4] not only silane but methane is also decomposed by the plasma and the reactions between the radicals of the two gases make the chemistry of the system very complicated. The physical properties of the material, which is then a complex carbon-silicon alloy, are quite different. In particular, it is possible to obtain high carbon concentrations in the films, up to 100% (open circles in Fig. 5). It is to be remarked that the same type of "high-power" material is produced, even at moderate powers, with a more easily decomposed gas like C_2H_6 or C_2H_2, which explains the rather high density of states of the material obtained with these gases.

In the low-power regime, not only the amount of carbon incorporated in the solid is limited to less than about 40%, but the concentration of hydrogen in the films can be very large. This is not surprising, since the most probable reaction between an active radical and CH_4 is bound to produce a methyl radical CH_3 or a methylated species R-CH_3. We can then expect that in the chemical model the carbon will be incorporated in the solid as a methyl group CH_3. This is clearly demonstrated in Fig. 6 where one can see that, from 0% up to 80% of methane, for each carbon atom in the solid, three hydrogen atoms are incorporated. The direct study of the methyl groups in the films by vibrational spectroscopy and nuclear magnetic resonance is under way and will be reported later.

Since the methyl groups CH_3 can only be terminators in the random network, they break the continuity of the amorphous network and one can expect the presence of microvoids or porosity in the films of methylated amorphouse silicon. This does not seem to be the case and, in fact, the material is quite compact and stable. The density of the material containing less than 20% of carbon, in accordance with a recent study on a material similar to ours,[18] is rather high and suggests a compact material. For example, the measured density of a film containing 10% of carbon (prepared with a gas mixture containing 60% of methane) is 2.0 g/cm^3, to be compared to a density of 2.25 g/cm^3 for a good quality hydrogenated amorphous silicon. This gives an average volume occupied by each CH_3 group of about 1.7 times the volume of a silicon atom, which is quite compatible with the absence of voids. Another argument for the absence of porosity is the very good stability of the material: A series of films with a carbon content ranging from 0% to 24% have

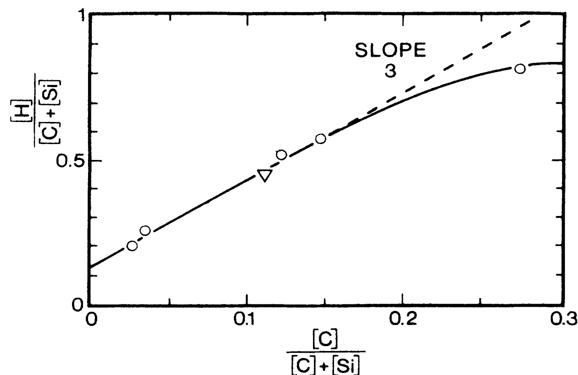

FIG. 6. Atomic concentration of hydrogen in the films as a function of the carbon incorporation. Up to 20% concentration of carbon (corresponding to a 80% proportion of methane in the gas phase), for each carbon atom three hydrogens are incorporated in the solid. This strongly suggests that in the low-power regime the incorporation of carbon is mostly in the form of methyl groups CH_3. The points (○ and ▽) correspond to the samples of Fig. 5.

shown exactly the same optical properties after 22 months of storage in atmosphere, which excludes the possibility of a deep oxydation.

IV. CONCLUSION

We have made a systematic study of the deposition and the physical properties of amorphous silicon-carbon alloys produced by glow discharge from silane-methane mixtures. We have defined a regime of preparation where the deposition processes are much simplified and therefore easier to control. In this "low-power regime," there is no primary decomposition of the methane, and the carbon is only incorporated in the solid by chemical reaction of the active radicals, produced by decomposition of the silane, with the methane. In this mode of preparation, the chemistry of deposition is separated from the complicated chemistry of the plasma thanks to the large difference in the decomposition thresholds between the two gases. The material produced possesses some remarkable properties which make it useful both as an exemplary alloy for materials research[2] and as a wide-gap semiconductor for applications to solar cells and other devices.[13]

(i) There is a smooth incorporation of carbon in the amorphous silicon network, giving an alloy with good semiconducting properties as verified, for example, by the low density of states in the mobility gap.[12]

(ii) The physical properties, in particular the optical properties (optical gap, refractive index) are very insensitive to the deposition conditions, depending mostly on the methane-to-silane ratio. This is not the case for the material produced at high power[4] which has properties depending not only upon the gas composition but also on the deposition conditions.

This is also the case for silicon-carbon alloys produced with a gas less stable than methane, like C_2H_6 or C_2H_2. These gases have decomposition thresholds that are comparable to that of silane: In this case, there is no low-power regime of deposition and the material produced has a high density of states in the gap.

(iii) Due to the "chemical" incorporation of carbon, the material produced in the low-power regime can only contain a limited amount of carbon. Even for a mixture of more than 90% of methane, the carbon concentration in the solid cannot be larger than 40%. This is not the case in the high-power regime where silicon-carbon alloys can be produced with arbitrary C-to-Si proportions.

(iv) Finally in our chemical model, the carbon is incorporated in the solid in the form of the methyl group CH_3, resulting in a material containing a large proportion of hydrogen. For this reason, it might actually be more proper to call the amorphous silicon-carbon alloys produced in the low-power regime "methylated amorphous silicon" $a\text{-}Si_{1-x}(CH_3)_x$:H or a-Si:CH_3:H.

ACKNOWLEDGMENTS

We wish to thank, for their invaluable help, Ms. M. Rommeluère (CNRS, Bellevue) for the microprobe analysis, Dr. C. Senemaud (University of Paris–VI) for the XPS measurements, and Dr. Meras (Service Central d'Analyse, Vernaison) for the chemical determination of the concentrations in the films. This work has been partially supported by the European Community Contract No. EN3S-0062-F(CD).

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We are grateful to the company SOLEMS S.A. for the permission to use their machine, and to Dr. Roubeau for the preparation of the films.

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