ISSN 1330–0008
CODEN FIZAE4

THERMAL STABILITY OF AMORPHOUS SILICON–CARBON ALLOYS DEPOSITED BY MAGNETRON SOURCE

DAVOR GRACIN, NIKOLA RADIĆ, UROŠ V. DESNICA, ŽELJKO ANDREIĆ and DAVOR BALZAR

Rudjer Bošković Institute, POB 1016, Bijenička 54, 10000 Zagreb, Croatia

Received 7 April 1995

UDC 539.215

PACS 68.60.Dv

Amorphous a$-$Si$_{0.85}$C$_{0.15}$:H and a$-$Si$_{0.6}$C$_{0.4}$:H alloys were deposited onto a non–heated substrate using a magnetron source. The samples were exposed to a sequential iso–chronal thermal annealing up to 1000 °C in a vacuum chamber, and were investigated by the IR spectroscopy and X-ray diffraction measurements. The influence of the thermal treatment on structural ordering was monitored by the evolution of the intensity and shape of the spectral IR lines corresponding to the Si$-$H and Si$-$C bonds. At low temperatures, the most pronounced features were accompanied with hydrogen evolution which completes up to 400 °C. Up to 800 °C the Si$-$C absorption lines have gradually changed their shape, peak position and intensity. At 900 °C, the abrupt changes occured, denoting final transition to crystalline state.

1. Introduction

The amorphous hydrogenated silicon–carbon alloy draws much attention as a potential material for optoelectronic devices [1]. Its thermal stability seems to be important for possible wider applications.

The crystallization process of a$-$Si$_{1-x}$C$_x$:H has been investigated in a somewhat different way, i.e. its dependence on carbon concentration [2]. Thus, two different concentrations have been chosen, the "low" with $x = 0.2$ and the "near stoichiometric" with $x = 0.4$.

It has been estimated that the a–$Si_{1-x}C_x$:H films contained certain amount of voids, the volume contribution of which is close to 20 vol % at $x \approx 0.15$, and more than 25 vol.% at $x \geq 0.4$ [3,4]. The volume of each void ranges from 2 to 7×10^{-22} cm^3, being larger for higher carbon content [3,4]. Besides, the Raman measurements performed on the a–$Si_{1-x}C_x$:H samples, deposited in similar condition as the samples reported here, indicated the presence of a certain amount of small carbon agglomerates [5]. Our discussion of experimental results will partly be based on these two facts.

2. Experimental

The amorphous hydrogenated silicon and silicon−carbide films, 1 μm thick were deposited by DC magnetron sputtering on the non−heated monocrystalline silicon substrate. The discharge was performed in an argon−hydrogen gas mixture with the addition of benzene vapour. The range of carbon alloying fraction was obtained by varying the benzene vapour pressure.

The IR transmittance measurements were performed using a Perkin−Elmer 2000 FTIR spectrometer. The obtained spectra were converted into absorption spectra by standard methods [6]. The deconvolution of absorption bands was done by least square fit method, assuming Gaussian intensity distribution for amorphous and Lorentzian distribution for crystalline samples.

The hydrogen content, C_{H}, was obtained from the integral absorption in the wagging-twisting-rocking band of the IR spectra, using the value of $1.6 \cdot 10^{19}$ cm^{-2} as a proportionality constant [7]. The hydrogen concentration in both samples was almost the same, ranging from 15 to 20 at%.

The carbon content, C_{C}, was estimated by Auger spectroscopy and IR absorption.

The sample annealing was performed in a vacuum chamber with a residual gas pressure of $\leq 5 \cdot 10^{-4}$ Pa. The samples were heated stepwise, sequentially, in the range of 180 °C to 1000 °C, with each annealing step lasting for 30 min.

3. Results

The IR absorption spectra of as deposited magnetron sputtered amorphous silicon carbide exhibit the usual absorption bands related to Si−H and C−H bonds (Table 1).

The oxygen features, also found in our samples, are related to the surface contamination which, as verified by Auger spectroscopy, does not penetrate deeper than $5 - 10$ nm. Each absorption line was broadened and the lines overlaped, thus making the exact analysis rather difficult. For the purpose of qualitative analysis, the relative weak bands in the 500 – 1200 cm^{-1} range have been neglected and the spectrum was deconvoluted into 3 bands: the Si−H related (640 – 670 cm^{-1}), Si−C related (720 – 800 cm^{-1}) and oxygen related (940 – 1100 cm^{-1}) bands.

TABLE 1.
Characteristic vibrational modes for sputtered a−Si_{1-x} C_x : H *[8].*

wave number /cm^{-1}	assignment
630-670	SiH_m, (m =1,2,3) wagging, twisting vibrations
720-800	Si−C stretching vibrations
780-800 (weak)	Si−O stretching vibrations
845-910 (weak)	SiH_m (m =1,2,3) bending, scissoring vibrations [9]
870-1070 (weak)	rocking, waging $(CH_m)_n$C Si (m =2,3; n =1,2,3)
940-1030	Si−O stretching vibration [9]
2000-2140	SiH_m, (m =1,2,3) stretching vibration [10]
2800-3000	CH_m stretching mode

The position of the absorption line related to the Si−C bonds is close to 720 cm^{-1} for dominant contribution of Si–Si_3C atom groups. The domination of C-C_3Si atom groups shifts the vibration frequency towards 800 cm^{-1} [8,9].

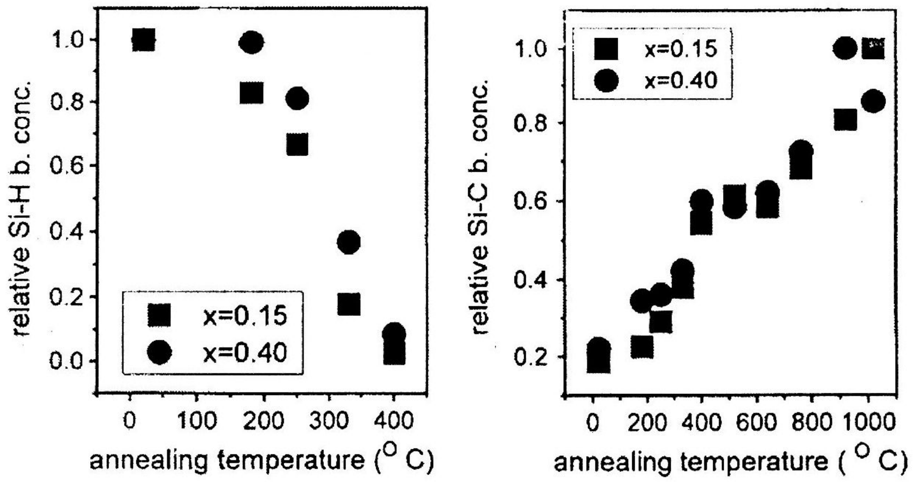

Fig. 1. Relative Si−H *bond concentration (a) and relative* Si−C *bond concentration (b) in* $Si_{1-x}C_x$:H *films versus annealing temperature for x=0.15 (squares) and x=0.4 (circles).*

Due to the annealing procedures, the IR spectra changed. At low temperatures, i.e. up to 400 °C, the vibration modes corresponding to the Si−H bonds decrease.

This decrease is similar in both samples, as shown in Fig. 1a where the relative Si−H bond concentration is plotted versus annealing temperature. At temperatures higher than 400 °C, the absorption bands related to the Si−H bonds disappear. The same dependence on annealing temperature is observed in the absorption attributed to the C−H stretching vibration (ranging from 2800 to 3000 cm^{-1}).

Within the same temperature interval, i.e. from the room temperature up to 400 °C, the absorption band corresponding to the Si−C bonds increases as seen in Fig. 1b in which the integrated absorption of the Si−C stretching bands, normalised at maximum intensity, is plotted versus annealing temperature. Further increase in annealing temperature in the range from 400 to 640 °C causes no changes in the Si−C bond concentration. Above this temperature region, up to 1000 °C, the Si−C bond concentration for $Si_{0.85}$ $C_{0.15}$ (squares in Fig. 1b) increases gradually.

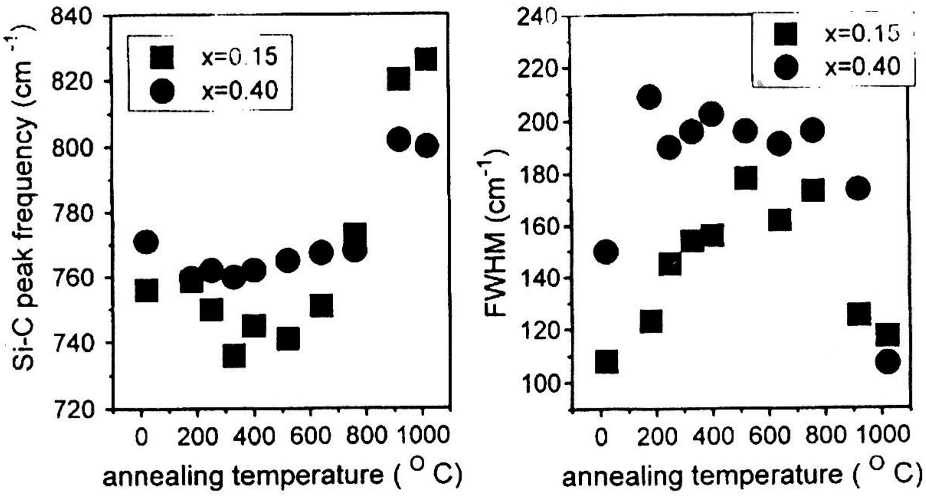

Fig. 2. The peak frequency (a) and the full width at half maximum (FWHM) of Si−C *absorption band in* $Si_{1-x}C_x$:H *films versus annealing temperature for* $x = 0.15$ *(squares) and* $x = 0.4$ *(circles).*

For $Si_{0.6}$ $C_{0.4}$ the Si−C bond concentration increases gradually up to 900 °C (circles in Fig. 1b). The number of Si−C bonds decreases above this temperature.

The peak frequency of the Si−C absorption band, plotted in Fig. 2a versus annealing temperature, changes almost equally for both samples. Up to 400 °C, the peak frequency slightly decreases, while above this themperature, close to 800 °C, it increases.

The changes are more pronounced in the sample with lower carbon concentration (squares in Fig. 2a) if compared to the "near stoichiometric" sample (circles in Fig. 2a). In the temperature range 800 °C to 1000 °C, the peak frequency of both samples changes abruptly.

In Fig. 2b the full width at half maximum (FWHM) of the C−H absorption line is plotted versus annealing temperature. For both samples, the value of FWHM increases up to 400 °C. Above this temperature, the width of the absorption line slightly lowers irregularly, up to 800 °C. Above this temperature, the width of the absorption line decreases rapidly for both samples.

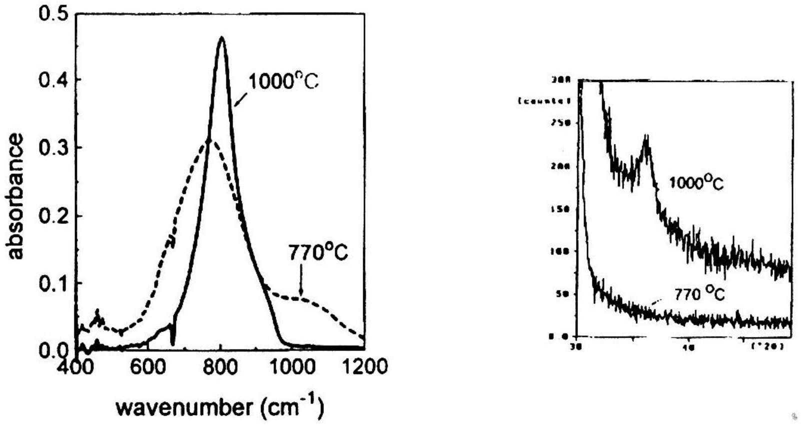

Fig. 3. The Si$-$C *absorption band (a) and the X$-$ray diffraction patterns (b) of the* $Si_{0.6}C_{0.4}$ *sample annealed in two successive steps, at 770* °C *and 1000* °C.

The marked change in the peak position and the width of the absorption line is accompanied by the apparent change in the absorption peak shape, as illustrated in Fig. 3a. In Fig. 3a, Si$-$C absorption band for $Si_{0.6}C_{0.4}$ sample, after annealing at two characteristic temperatures, is presented. The absorption line measured after annealing at 770 °C (dashed curve in Fig. 3a) has Gaussian shape while the second one (solid curve in Fig. 3a) is more like Lorentzian. This change in the peak shape indicates the formation of a crystalline phase [11, 12]. This statement is well supported by X$-$ray diffraction measurements, illustrated in Fig. 3b, in wich the X$-$ray diffraction patterns of $Si_{0.6}C_{0.4}$, annealed at two successive steps, are plotted. The lower curve in Fig. 3b was measured after annealing at 770 °C, and it corresponds to the Gaussian line shape of the IR absorption line in Fig. 3a. The upper curve in Fig. 3b, measured after annealing at 1000 °C, corresponds to the Lorentzian line shape in IR (see Fig. 3a). The broad X-ray diffraction line close to ca. $2\theta = 36^0$, clearly distinguishable in the upper diffraction pattern, confirms the presence of small cubic SiC crystallites, about 10 nm in size.

4. *Discussion*

A simple model from Ref. 7 is adopted in our discussion of the results. The a$-Si_{1-x}C_x$:H is assumed to consist of a network of silicon and carbon atoms interrupted by voids. The internal surfaces of voids are decorated with hydrogen and certain but small amount of CH_x atom groups. The volume contribution voids and sizes of voids increase with hydrogen and carbon concentration [12]. Furthermore, the voids are large enough to accommodate the C_mH_n groups. This carbon−hydrogen agglomerate, observed by Raman spectroscopy [5] in samples deposited under the conditions similar to those reported here, are possibly due to the incomplete or late dissociation of benzene molecule during the film formation.

According to this model, the first increase in the Si−H bonds concentration, up to 400 °C, can be explained by the replacement with Si−C bonds of the Si–H bonds. Hydrogen effuses through the voids out of the sample, and carbon, present in the voids, is bonded to free silicon atoms at the voids internal surfaces. In the sample with a low carbon content ($x = 0.15$), close to the voids internal surfaces mostly the silicon atoms are present, and the new Si−C bond is in a silicon rich matrix, with corresponding frequency close to 720 cm^{-1}.

Thus, the observed decrease of the peak frequency (squares in Fig. 2a), from as deposited 755 cm^{-1} towards 730 cm^{-1} as the annealing temperature increases up to 400 °C, can be explained. For the sample with higher carbon content, the surrounding of voids consists of mixed Si and C atoms, and the frequency of new bonds should be around 760 cm^{-1}. For the $Si_{0.6}$ $C_{0.4}$ sample, the starting frequency is around 770 cm^{-1} and the new Si−C bonds, with the corresponding frequency of ca. 760 cm^{-1} again lowers the peak frequency.

In the range of 400 to 800 °C, there are only a few new Si−C bonds. Silicon and carbon atoms diffuse through the matrix. The change in the width of the Si−C absorption line is small (Fig. 2b), as well as the change in the peak position for $Si_{0.6}C_{0.4}$ (circles in Fig. 2a). However, for the $Si_{0.85}$ $C_{0.15}$ sample, there is an increase in the peak frequency (squares in Fig. 2a). One of the possible reasons for more pronounced changes in the silicon rich, e.g. $Si_{0.85}$ $C_{0.15}$ sample, is the difference in bond energies, which are 1.8 and 3.0 eV for Si−Si and Si−C, respectively, resulting in different diffusion constants. Furthermore, the diffusion of silicon atoms through the small voids, vacancy or divacancy, in crystalline silicon requires very low energy. In amorphous silicon matrix, similar effects are expected.

5. *Conclusion*

The results of successive annealing of the a−$Si_{1-x}C_x$:H samples causing changes from the amorphous to crystalline state, can be divided into the three temperature intervals.

At low temperatures, the most pronounced feature is the hydrogen effusion, which is completed up to 400 °C. The new Si−C bonds appear and disorder in material increases (the width of the absorption lines increases).

In the range from 400 to 800 °C, there are only a few new Si−C bonds. The process of ordering is weak due to the high activation energy for diffusion. In $Si_{0.85}$ $C_{0.15}$, the diffusion is somewhat more pronounced than in $Si_{0.6}$ $C_{0.4}$ due to the lower energy for diffusion in a Si matrix compared to the one in a Si−C matrix. The presence of small voids in the $Si_{0.85}$ $C_{0.15}$ sample most probably enhances the Si atom diffusion.

In the range of 800 to 1000 °C, the crystallization occurs. It is observed by FTIR and X−ray diffraction measurements. The crystallites in $Si_{0.6}$ $C_{0.4}$ sample were estimated at 10 nm in size. In $Si_{0.85}$ $C_{0.15}$ samples, the crystallites are probably smaller and embedded in a polycrystalline Si matrix.

References

1) H. Ruebel, J. Foelsh and H. Shade, Solid State Comm. **85** (1993) 593;

2) K. Yoshii, Y. Suzaki, A. Takeuchi, K. Yasutake and H. Kawabe, Thin Solid Films **199** (1991) 85;

3) D. Gracin, N. Radić and U. V. Desnica, to be published in Vacuum;

4) D. L. Williamson, A. H. Mahan, B. P. Nelson and R. S. Crandall, Appl. Phys. Lett. **55** (1989) 783;

5) S. Lugomer, M. Ivanda, D. Gracin, K. Furić and A. Maksimović, J. Mol. Structure **276** (1992) 347;

6) M. H. Brodsky, M. Cardona and J. J. Cuomo, Phys. Rev. **B16** (1977) 3556;

7) D. Gracin, U. V. Desnica and M. Ivanda, J. Non-Cryst. Solids **149** (1992) 257;

8) H. Ruebel, B. Schroeder, W. Fuhs, J. Krauskopf, T. Rupp and K. Bethge, Phys. stat. sol. (b) **139** (1987) 131;

9) J. C. Knights, G. Lucovsky and R. J. Nemanich, J. Non-Cryst. Solids **32** (1979) 393;

10) G. Lucovsky, J. Yang, S. S. Chao, J. E. Tyler and W. Czubatayj, Phys. Rev. **B 28** (1983) 3225;

11) D. K. Basa and F. W. Smith, Thin Solid Films **192** (1990) 121;

12) S. Inoue, K. Yoshii, M. Umeno and H. Kawabe, Thin Solid Films **151** (1987) 403;

13) D. Gracin, M. Ivanda, S. Lugomer, N. Radić and U. V. Desnica, Appl. Surf. Sci. **70 71** (1993) 686.

TERMIČKA STABILNOST SILICIJ–UGLJIK AMORFNIH LEGURA NANEŠENIH MAGNETRONSKIM IZVORIMA

Slojevi amorfnog a−$Si_{0.85}C_{0.15}$:H i a−$Si_{0.6}C_{0.4}$:H su formirani magnetronskim izvorom, na nezagrijanoj podlozi. Nakon depozicije, uzorci su postepeno grijani u vakuumu do 1000 °C. Između uzastopnih grijanja vršena su mjerenja infra–crvenom spektroskopijom i difrakcijom X-zraka. Utjecaj ovakvog termalnog tretmana na strukturno uređenje uzoraka je praćeno razvojem intenziteta i oblika spektralnih linija koje odgovaraju Si−H i Si−C vezama. Na nižim temperaturama, najizrazitije promjene su vezane za desorpciju vodika, koja završava do 400 °C. Daljnjim grijanjem do 800 °C, linije postepeno mijenjaju oblik, intenzitet i frekvenciju maksimuma. Grijanje na i iznad 900 °C uzrokuje nagle promjene, označavajući prijelaz u kristalinično stanje.