STRUCTURE OF a-Si:H/a-$Si_{1-x}C_x$:H MULTILAYERS DEPOSITED IN A REACTOR WITH AUTOMATED SUBSTRATE HOLDER

J. Bertomeu, J.M. Asensi, J. Puigdollers, J. Andreu and J.L. Morenza.
Universitat de Barcelona, Departament de Física Aplicada i Electrònica.
Av. Diagonal 647, E-08028 Barcelona, Spain.

ABSTRACT

This paper deals with the structural properties of a-Si:H/a-$Si_{1-x}C_x$:H multilayers deposited by glow-discharge decomposition of SiH_4 and SiH_4 and CH_4 mixtures. The main feature of the rf plasma reactor is an automated substrate holder. The plasma stabilization time and its influence on the multilayer obtained is discussed. A series of a-Si:H/a-$Si_{1-x}C_x$:H multilayers has been deposited and characterized by secondary ion mass spectrometry (SIMS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). No asymmetry between the two types of interface has been observed. The results show that the multilayers presents a very good periodicity and low roughness. The difficulty of determining the abruptness of the multilayer at nm scale is discussed.

I. Introduction

Since Abeles and Tiedje[1] reported in 1983 the first results on deposition and characterization of hydrogenated amorphous silicon based multilayers, there have been important advances in this field. Applications of amorphous semiconductor multilayers have been reported: thin film transistors (TFT)[2], solar cells[3], avalanche photodiodes (APD)[4], phototransistors[5] and electroluminiscent devices[6]. Although these structures have improved their performance, much effort is still necessary to optimize the technological process and understand the properties of these materials.

Several techniques have been used in amorphous semiconductor multilayer deposition: plasma assisted chemical vapor deposition (PACVD), photo-CVD, reactive sputtering and evaporation. The best results have been obtained in PACVD and photo-CVD deposited multilayers. These two techniques have been extensively studied in a-Si:H and related alloy deposition, so their technology is well known. The main problem in PACVD deposited multilayers is to obtain good interfaces and uniform periodicities, so non-aggressive plasma conditions, an optimized exchange of reactive gases and stable conditions of the plasma are required. To optimize the exchange of reactive gases there are different methods: some groups have minimized the residence time compared to the time required to grow a monolayer, without switching off the plasma[1]; others prefer to switch off the plasma and pump down the chamber to eliminate cross-contamination[7]; other groups have used a two-chamber reactor and the substrates are exposed alternatively to two different plasmas[8]. In this paper, we present an alternative solution which is technically simple and has allowed us to obtain high quality structures. The main feature of this deposition system is an automated rotating substrate holder, enabling the removal of the samples from the plasma during the gas exchange period and plasma stabilization.

The present paper is devoted of the structural characterization of a-Si:H. In addition of the structural parameters of each bulk material, several concepts have to be considered to study the structural characteristics of the multilayers. The first is the uniformity of the periodicity along the whole structure. Another is the roughness of the interfaces. Finally, the abruptness in the composition changes at the interfaces. In order to obtain these parameters, a-Si:H/a-$Si_{1-x}C_x$:H multilayers have been characterized by secondary ion mass spectrometry (SIMS), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

II. Experimental set up

The samples were deposited in an RF capacitively coupled reactor used for the deposition of a-Si:H based alloys and devices. The pumping equipment consists of a turbomolecular pump, a Roots pump and a rotatory pump. There are eight different gas lines (SiH_4, GeH_4, PH_3, B_2H_6, CH_4, NH_3, H_2 and N_2) with pneumatic valves and mass flow controllers. The vacuum vessel is a stainless steel cylinder of 30 cm diameter. The substrates are placed on a grounded plate in contact with a heater. This plate can rotate over another grounded plate, allowing us to expose one, two, three or four substrates to plasma. This feature is very useful for obtaining different thicknesses of the same material. The movement of the substrate holder is provided by a stepping motor through a magnetically coupled motion transmission and a epicycloidal gear, designed and constructed in our laboratory. In Figure 1 there is a view of the substrate holder and the plasma chamber. The deposition system is completed by an RF power supply (13.56 MHz) and an automatic matching network. The valves, flow rates, pressures and the movement of the substrate holder are controlled by a personal computer.

The samples used in this study consist of a series of 6 multilayers, all of them with the same a-$Si_{1-x}C_x$:H layer thickness and different a-Si:H layer thicknesses and number of layers (Table I). The technological parameters used in the multilayers reported here were a pressure of 20 Pa, a substrate temperature of 300°C, an RF power of 5 W (27 mW/cm^2), and a gap between electrodes of 4 cm. Gas flow was maintained at 20 sccm. Pure silane was used in a-Si:H layer deposition, while a-$Si_{1-x}C_x$:H was deposited from a mixture of silane (1 sccm) and methane (19 sccm). Composition of the a-$Si_{1-x}C_x$:H layers was estimated from XPS measurements as $x = 0.4$. Self bias was measured as 56 V in a-Si:H layers and 59 V in a-$Si_{1-x}C_x$:H layers. The deposition rates of the materials, measured from individual layers, were 4.20 nm/min for a-Si:H and 3.24 nm/min for a-$Si_{1-x}C_x$:H. Three different substrates were used: c-Si wafers, Corning 7059 glass and KBr substrates.

The deposition process was automated, so the deposition time and the periodicity in plasma composition were totally controlled. The plasma was maintained continuously but the substrates were hidden during the gas exchanging process, and exposed again when the pressure, flow rates and self bias were stable.

SIMS depth profiles were obtained using an ATOMIKA A-DIDA 3000-30 spectrometer. The primary beam consisted of 4 KeV O_2^+ ions and a 200 nA beam current, and electron bombardment was used for charging compensation. The crater size was 900 μm × 900 μm and a gate of 20 % was selected.

Low-angle X-ray ($\lambda = 1.54$ Å) diffraction patterns were obtained from a SIEMENS D500 powder diffractometer, using a special sample holder which allows micrometrical vertical shifts in order to align the sample correctly.

TEM micrographs were obtained in a HITACHI H-800-MT microscope. The samples were prepared using a KBr substrate. A resin was deposited over the multilayer. The substrate was then dissolved in water and the multilayer and the resin layer were embedded in epoxy resin. The resin was polymerized at 60°C for 48 hours. Finally, the whole block was cut by ultramicrotome in 70-90 nm sections, which were picked up with a copper grid. This technique of preparation is very common in biological samples but has not been reported in this type of materials.

III. Technological considerations.

The quality of amorphous silicon-based multilayers deposited by PECVD depends on the deposition conditions, which must be considered in detail. The best results were obtained with a low RF power and in the α-regime of the plasma[9], producing low growth rates.

In order to obtain a well-defined interface it is also necessary to control the process of change from the silane to a silane/methane mixture discharge. When depositing multilayers by fast switching of feeding gases, it is necessary to minimize residence times of the gases in order to stabilize the gas phase stoichiometry rapidly. However, this does not guarantee homogeneous deposition conditions throughout growing layer. The self bias monitoring during the gas exchange process has shown us that the transients in the plasma conditions from the SiH_4 + CH_4 mixture to pure SiH_4 is fast (a few seconds after pressure and fluxes became stable), whereas the transient from SiH_4 to the mixture is slower (approximately one minute after pressure and fluxes became stable). This result agrees with Fischer et al.[10], who have studied these transients by measuring the light intensity of the plasma. This behavior can be attributed to the difficulty in ionizing the methane at low power. This ionization is only produced by secondary processes[11], and a considerable time is required to stabilize the plasma. The separation of the substrates from the influence of the plasma during the exchange process is thus very important in order to avoid the possible effect of these transients on the interface quality. By monitoring the self bias values, the time necessary to obtain abrupt interfaces can be optimized.

In order to demonstrate the total elimination of cross contamination due to the use of single chamber, two layers, one of a-$Si_{1-x}C_x$:H and other of a-Si:H were sequentially deposited in the same run with the analogous procedure used to deposit multilayers, but each one on a crystalline substrate. The SIMS analysis of the a-Si:H layer did not show the presence of C, demonstrating that problems of non-abrupt composition change at the interfaces are related to the interaction of the growing layer with the previous layer, which also occurs in the multichamber reactors.

The monitoring of self bias enables us to control the conditions in which the process is stable. Plasma becomes unstable and hysteresis occurs at certain conditions, for example in the proximity of plasma transition observed at pressures above 20 Pa[9,12,13]. In these cases appreciable changes in self bias are observed. The recovery of the reactor wall by the growing film also influences the deposition conditions, especially in the higher pressure deposition regime. These changes produce fluctuations in the deposition rate and have disturbing consequences for the periodicity of the multilayer obtained.

IV. Results and Discussion

The thicknesses of the multilayers were measured by different techniques: direct measurement by TEM of cross sections, layer spacing obtained from X-ray diffraction and total thickness measurement by a Dektak 3030 profiler. The measurement of layer spacing and total thickness allowed the calculation of deposition rates for both materials, since the thickness of a-$Si_{1-x}C_x$:H layers is the same in all the samples (Figure 2). The agreement between these results and the thicknesses expected from the deposition rates of both materials is very good, as can be seen in Table I.

SIMS depth profiles of a-Si:H/a-$Si_{1-x}C_x$:H multilayers were obtained for all the samples, showing a modulation in hydrogen and carbon content. In samples #5 and #6 the periodicity could not be resolved by this technique because of the mixing produced by the ion bombardment. A typical SIMS depth profile is shown in Figure 3. Hydrogen modulation was observed in multilayers with periodicity of 10 nm. In multilayers with lower periodicities, no modulation was observed.

The quantification of SIMS profiles is very difficult because of the absence of suitable patterns for these materials due to the great influence of the technological parameters on the amorphous matrix, which can induce changes in the ionization yields which are greater than the effect of changes in the composition.

A common feature of all the depth profiles is a difference between the positions of the $^{1}H^{+}$ maxima and the positions of the $^{12}C^{+}$maxima. The maximum hydrogen content appears before the maximum carbon content. This fact suggests an asymmetry between the interfaces due to differences in the diffusion coefficients for hydrogen in both materials during the growth process. This explanation was offered by Hundhausen et al.[14] for n-i-n-i multilayers, and it would imply a higher diffusion coefficient of hydrogen in a-$Si_{1-x}C_x$:H. However, this asymmetry could also be due to differences between the implantation depth of atoms present during the ion bombardment process, related to differences between the densities of both materials. To examine this hypothesis, we deposited a 50 nm a-$Si_{1-x}C_x$:H layer between two

50 nm a-Si:H layers, and we performed two SIMS depth profiles, the first in the usual way, and the second starting from the first a-Si:H layer, after removing the sample from the substrate. The results are shown in Figure 4: the shape of the profile is the same in both cases, although in the second case a reduction in the contrast is observed due to the process of removing the sample from the substrate. We can thus conclude that the asymmetry in SIMS depth profiles is due to an artifact of the measurement rather than to a possible asymmetry between the interfaces.

A shift to higher angles in the position of the peaks was observed in the XRD patterns. This displacement is greater when the position of the peak is at very low angles and becomes negligible for higher angles. So the layer spacing obtained from the first order is lower than that from the second and so on. The spectra were corrected assuming that this shift is due to the vertical divergence angle of the Soller slits in our diffractometer. This correction is considerable at very low angles in standard powder diffractometers[15]. The values for the layer spacing were calculated weighing all the diffraction orders detected. The layer spacings so obtained are shown in Table I. Although this correction has given good results, there may be other factors affecting this shift of the peaks, such as a small displacement of the sample in the vertical direction.

The X-ray diffraction pattern of sample #3 is shown in Figure 5. Up to fourth order reflection can be observed in this figure. The layer spacing determined from the method described previously is 10.9 nm, while the values obtained from the first, second and fourth reflections were 9.8, 10.4 and 10.8 nm respectively. The absence of the third order peak in this sample is due to the fact that the thickness of a-Si:H layer coincides approximately with twice the thickness of a-$Si_{1-x}C_x$:H layer. A significant parameter to characterize the quality of a multilayer is the full width at half maximum of the first order Bragg peak obtained from its rocking curve. A sharp peak indicates uniform periodicity, a consequence of a well defined deposition rate, and low interface roughness. Both effects, if present, produce a widening of the above-mentioned peak. It is meaningful to point out that a sharp peak does not indicate abrupt interfaces, because the theoretical calculated peaks for a sinusoidal compositional dependence are also sharp. The width of this peak for sample #3 is 0.013°, which is one of the lowest values reported for this type of multilayer. Periodicities lower than 4.5 nm were obtained with very sharp peaks (Figure 6). A quantitative estimation of the roughness can be obtained from the integrated values of the diffraction peaks with the treatment of Abeles et al.[16]. The simultaneous application of this treatment to all the samples measured in the presented series gives a roughness of 0.7 nm. Another estimation of roughness was carried out from the widths of the different reflection orders. The experimental widths increase in the same sample with the order of reflection, in contrast to the behavior expected from the previous model. The deviation from the mean value of the thickness can be derived from the Bragg law as a function of the width of the reflection orders:

$$\Delta d = -\frac{m\lambda}{2\sin^2\theta}\cos\theta\,\Delta\theta \qquad m = 1,\ 2,\ 3\ldots$$

With this treatment, approximately the same value for Δd was obtained from the different reflection orders of the same sample, and these values range in all the samples measured between 0.4 and 1 nm. These values are very close to the results of Chu et al.[17], who obtained a value of 1 nm for a-Si:H/a-$Si_{1-x}C_x$:H multilayers with a similar carbon content by *in situ* ellipsometry.

Cross sectional images of multilayers were obtained by TEM. Caution was necessary to obtain satisfactory results because the final step in the sample preparation process was not very precise. It was necessary to locate regions in the sample which were sufficiently thin to allow the passage of electrons, and the section had to be perpendicular to the multilayer plane. Nevertheless, good images of multilayers with low periodicities were obtained without difficulty. One advantage of this method is that the size of the zone that can be observed is larger than in samples prepared by other methods. In Figure 7, we show a micrograph of the zone near substrate of sample #4. It can be observed that the layers are smooth and uniform along the film and the periodicity is very good, but a small undulation appears in the top layers. This has also been reported by Schwarz et al.[10].

An estimation of the roughness of the individual layers in the structure of Figure 6 was obtained through the digitalization of a zone of the micrograph. The zone selected was a square of approximately 18.5 nm side. This zone has been digitalized in 4096 points, so every pixel corresponded to approximately 0.29 nm. This value is lower than the resolution of our microscope in optimal conditions. A contour level map of the optical density of a zone from Figure 7 can be seen in Figure 8. We calculated the roughness of the layers by mapping the pixels which have the mean value of the density of the maximum and the minimum. The width of the fringes where all the pixels corresponding to a same level of density are contained gives an estimation of the roughness. In our case, a maximum deviation of 0.6 nm from the mean was found, in agreement with XRD results.

However, this value can only be considered as an indicative parameter. In our opinion, the correct interpretation of this result is difficult, as the obtention of the image of an amorphous material in an electron transmission microscope is hindered since techniques usually used in crystalline materials, such the Fourier-plane filtering of the electron beam, are not applicable. The result could also be affected by the preparation of the sample for TEM observation, or by a slight deviation of the cross-section plane from the perpendicular to the electron beam in TEM observation. In this case, the high ratio between the electron path through the layer and the interlayer spacing, could produce an average of surface roughness, giving images of interfaces as if they were compositionally smooth. This effect is shown in Figures 7 and 8. Although roughness and abruptness are conceptually different, it is difficult to separate them.

We conclude that determination of the compositional abruptness of the multilayers presents the most difficulties. The amorphous character of multilayers of amorphous silicon and related alloys present supplementary problems in the determination of interface abruptness compared with their crystalline counterparts, and more efficient characterization techniques are necessary to improve their preparation technology.

V. Conclusions

The technological parameters relevant in the obtention of multilayers with good structural properties by the PACVD technique has been considered in detail. The monitoring of self bias voltage has allowed a correct determination of the waiting time necessary to stabilize the plasma before the deposition of the next layer. The analysis by SIMS of samples grown in the same run demonstrates that the cross contamination is eliminated. As a consequence, eventual smoothness in the compositional profile at the interfaces has been attributed to the plasma-enhanced mixing between the growing layer and substrate layer, also present in the best two-chamber reactors.

The structure of a series of a-Si:H/a-$Si_{1-x}C_x$:H multilayers has been studied by SIMS, XRD and TEM. Asymmetry in the positions of $^1H^+$ and $^{12}C^+$ maxima in SIMS depth profiles has been observed, but we have demonstrated that this asymmetry is probably due to a SIMS effect rather than to asymmetry between the two interfaces. The XRD results show that the multilayers present uniform periodicities and flat interfaces with low roughness, as can be deduced from the rocking curve sharpness. From the study of the cross-sections by TEM, a value lower than 0.6 nm has been obtained for the roughness at the interfaces. The TEM photographs present a non-abrupt dependence of image density, the interpretation of that as a consequence of an analog dependence of the compositional profile is not very clear, as an average of surface roughness along the electron path would produce a similar effect. This emphasizes the difficulties in the determination of compositional profile abruptness in amorphous multilayers.

Acknowledgements

We acknowledge the collaboration of the Scientific-Technical Services of the University of Barcelona, where XRD and TEM measurements were performed, and of Secondary Ion Mass Spectrometry Service of the University of Barcelona. We are also grateful to D. Binagui for his contribution to the substrate holder design and assembly. This work was supported by the DGICYT of the Spanish Government under program PB89-0236. One of the authors (J.B.) acknowledges partial support by CIRIT of the Generalitat de Catalunya (AR89).

References

[1]B. Abeles and T. Tiedje, Phys. Rev. Lett. **51**, 2003 (1983).

[2]M. Tsukude, S. Akamatsu, S. Miyazaki and M. Hirose, Jpn. J. Appl. Phys. **26**, L111 (1987).

[3]S. Tsuda, H. Tarui, T. Matsuyama, T. Takahama, S. Nakayama, Y. Hishikawa, N. Nakamura, T. Fukatsu, M. Ohnishi, S. Nakano and Y. Kuwano, Jpn. J. Appl. Phys. **26**, 21 (1987).

[4]S. C. Jwo, M.T. Wu, Y.K. Fang, Y.W. Chen J.W. Hong and C.Y. Chang, IEEE Trans. Electron Devices **35**, 1279 (1988).

[5]M.T. Wu, Y.K. Fang, J.W. Hong and C.Y. Chang, Solid-St. Electron. **32**, 189 (1991).

[6]G. Chen, F. Zhang and S. Yan, J. Non-Cryst. Solids **137&138**, 1263 (1991).

[7]S. Nishikawa, H. Kanikuma, T. Watanabe and K. Nihei, Jpn. J. Appl. Phys. **25**, 1141 (1986).

[8]J. Kakalios, Phil. Mag. B **54**, 199 (1986).

[9]J. Perrin, P. Roca i Cabarrocas, B. Allan and J.M. Friedt, Japan J. Appl. Phys. **27**, 2041 (1988).

[10]R. Schwarz, T. Fischer, P. Hanesch, T. Muschik, J. Kolodzey, H. Cerva, H.L. Meyerheim and B.M.U. Scherzer, Appl. Surf. Sci. **50**, 456 (1991).

[11]J. Bullot and M.P. Schmidt, Phys. Stat. Sol. (b) **143**, 345 (1987).

[12]J.L. Andújar, E. Bertran, A. Canillas, C. Roch and J.L. Morenza, J. Vac. Sci. Technol. A **9**, 2216 (1991).

[13]C. Böhm and J. Perrin, J. Phys. D: Appl. Phys. **24**, 865 (1991).

[14]M. Hundhausen, P. Santos, L. Ley, F. Habraken, W. Beyer, R. Primig and G. Gorges, J. Appl. Phys. **61**, 556 (1987).

[15]H.P. Klugg and L.E. Alexander, *X-ray Diffraction Procedures*, p. 256. John Wiley, New York (1954).

[16]B. Abeles, T. Tiedje, K.S. Liang, H.W. Deckman, H.C. Stasiewski, J.C. Scanlon and P.M. Eisenberger, J. Non-Cryst. Solids **66**, 351 (1984).

[17] V. Chu, M. Fang and B. Drevillon, J. Appl. Phys. **69**, 3363 (1991).

Figure Captions

Figure 1: Schematic view of the plasma chamber (top) and top view of the substrate holder (bottom).

Figure 2: Calculation of the deposition rates of both materials from the measured thicknesses of the elementary pair of layers. The deposition rates from the fit are 4.08 nm/min for a-Si:H and 3.42 nm/min for a-$Si_{1-x}C_x$:H.

Figure 3: SIMS depth profile of sample #1. $^{1}H^{+}$, $^{12}C^{+}$ and $^{29}Si^{+}$ ions are followed.

Figure 4: SIMS depth profiles of a 50 nm thick a-$Si_{1-x}C_x$:H layer between two a-Si:H layers performed in the usual way (right) and starting from the first layer deposited (left). The same asymmetrical shape is observed in both cases.

Figure 5: X-ray diffraction pattern vs scattering angle of sample #3. The inset shows the rocking curve of the first Bragg peak (f.w.h.m.: 0.013°).

Figure 6: X-ray diffraction pattern vs scattering angle of sample #6. The inset shows the rocking curve of the first Bragg peak (f.w.h.m.: 0.019°).

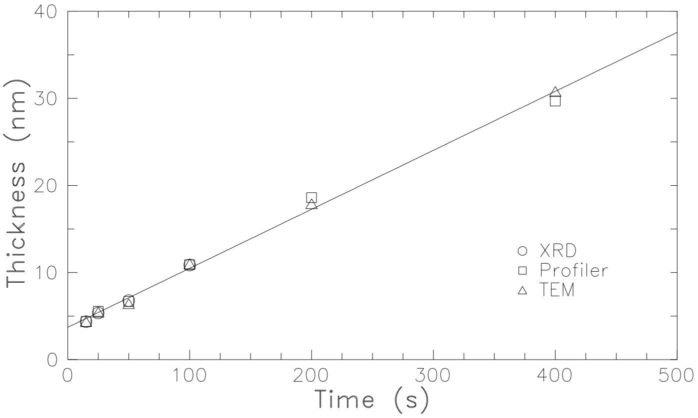
Figure 7: TEM photograph of sample #4 (a-Si:H layers in dark).

Figure 8: Contour level map of optical density of a zone in the photograph shown in Figure 7. From the deviation of a same level curve from its mean position, an estimation of the roughness has been obtained.

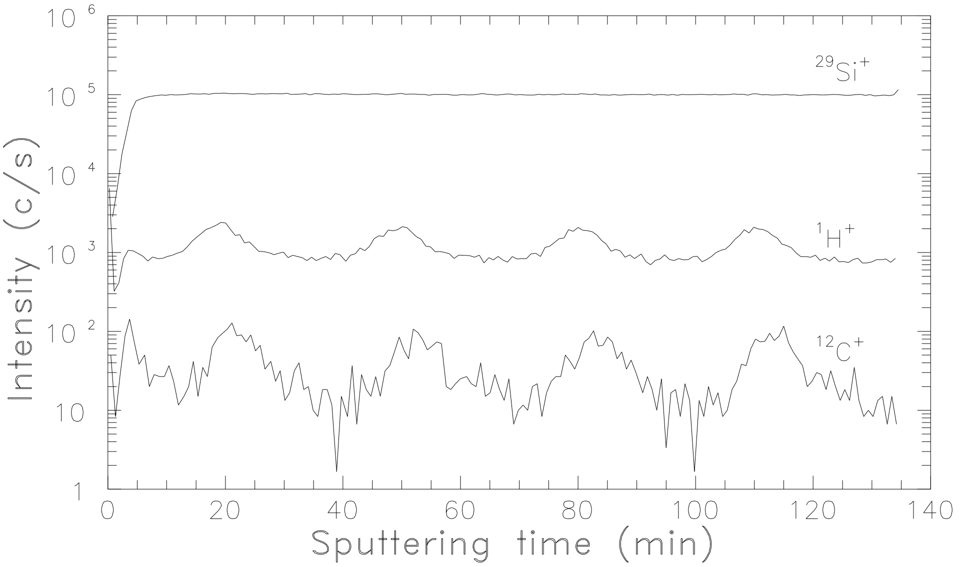
TABLE I. Parameters of the layers used in this study, expected thicknesses from the deposition rates of both materials and thicknesses of the elementary pair of layers measured by XRD, TEM and total thickness measurements with a profiler. t_s is the deposition time of each a-Si:H layer (for a-$Si_{1-x}C_x$:H layers this time is 65 s in all samples).

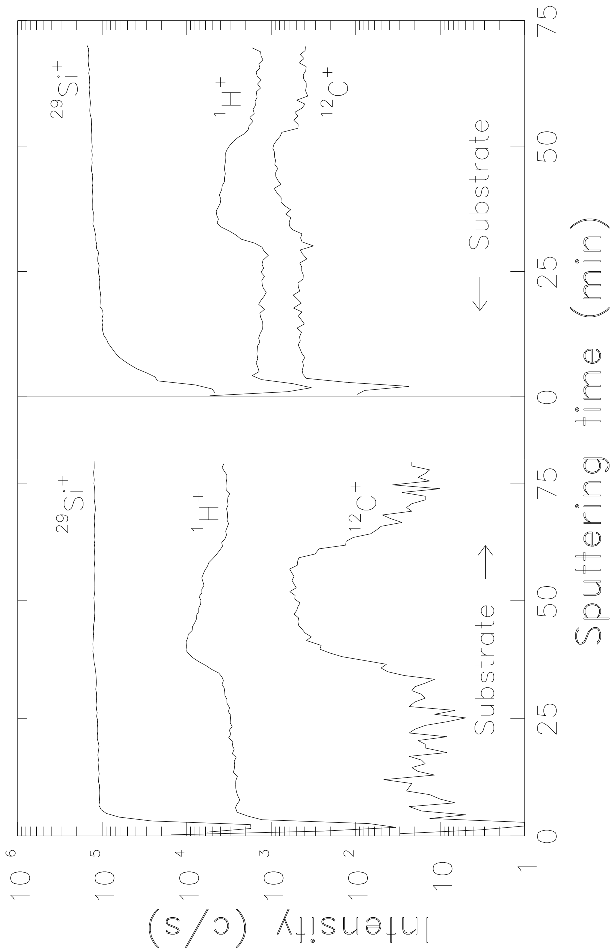
Sample	t_s (s)	Number of bilayers	Expected thickness (nm)	Measured thickness (nm)			
				XRD	TEM	Profiler	
						Layer	Total
#1	400	15	31.5	*	30.8	29.7	445
#2	200	25	17.5	*	17.9	18.6	464
#3	100	40	10.5	10.9	11.0	10.9	437
#4	50	60	7.0	6.8	6.4	6.7	400
#5	25	80	5.3	5.6	5.5	5.6	445
#6	15	100	4.3	4.4	4.4	4.4	440

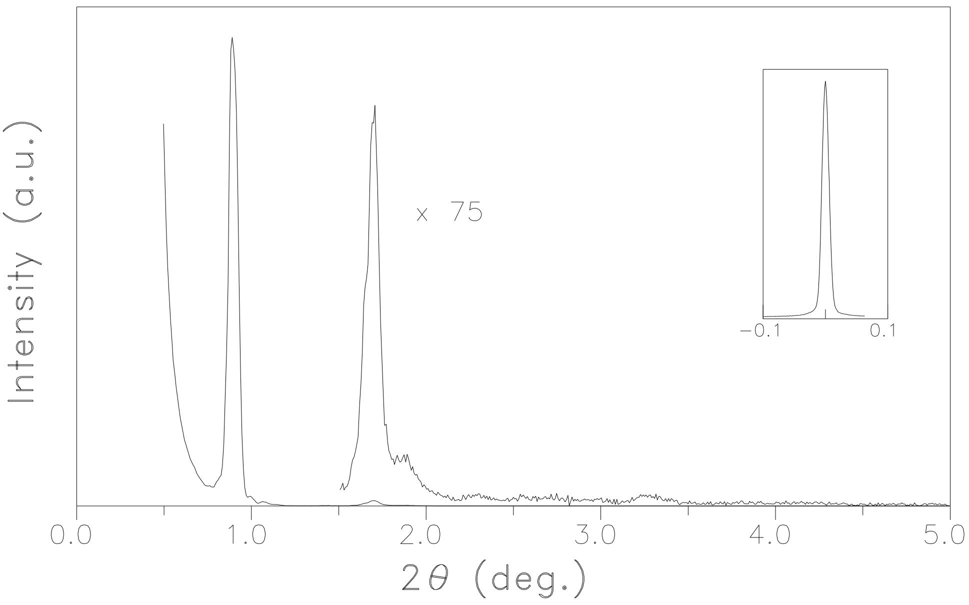
* Not measured



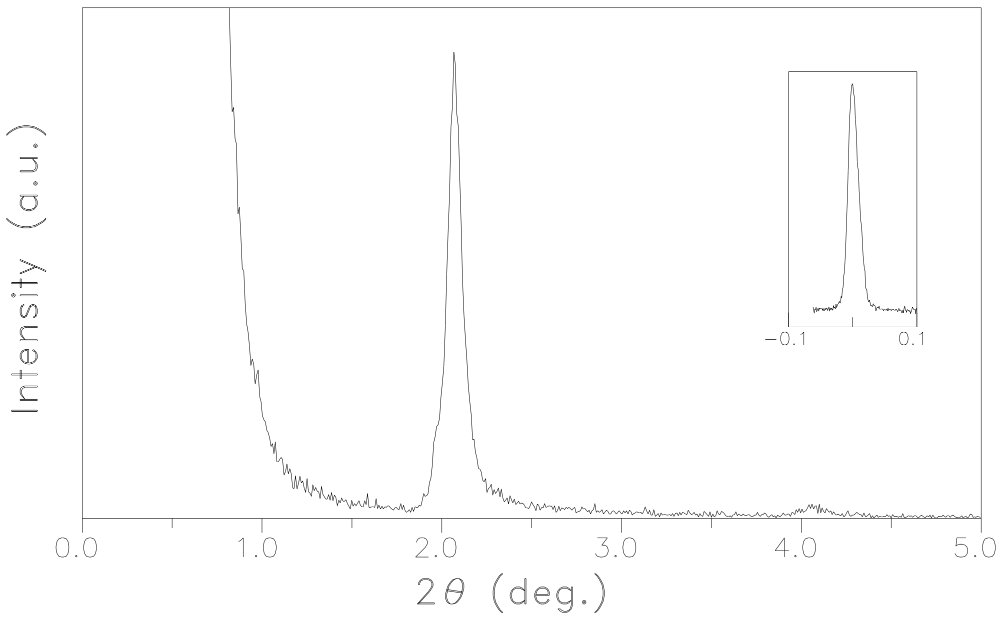
Thickness (nm)
Time (s)
0
10
20
30
40
0
100
200
300
400
500
○ XRD
□ Profiler
△ TEM

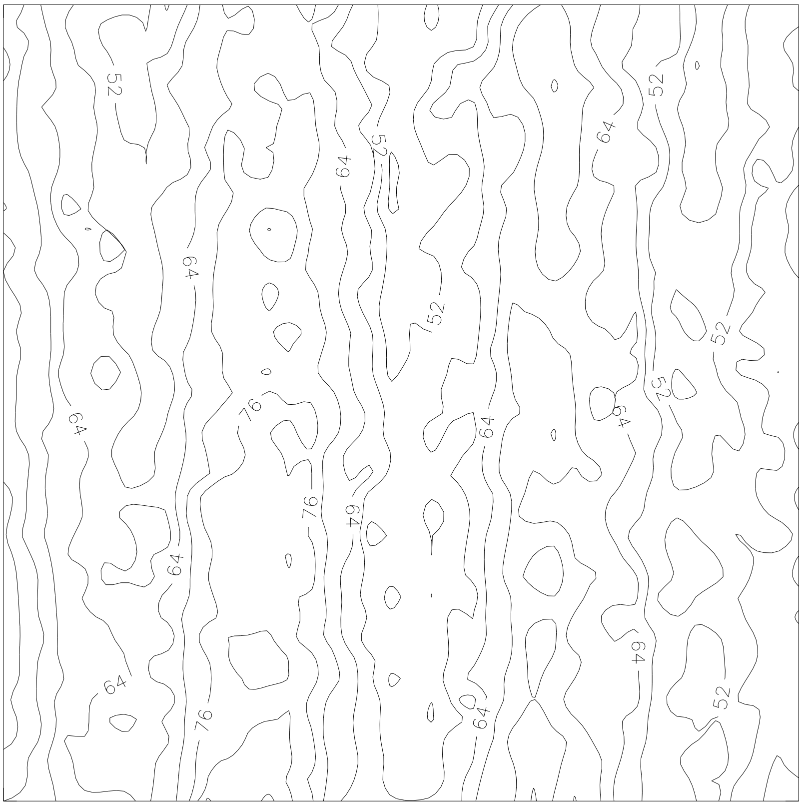

10^6
10^5
10^4
10^3
10^2
10
1
Intensity (c/s)
$^{29}Si^+$
$^1H^+$
$^{12}C^+$
0
20
40
60
80
100
120
140
Sputtering time (min)


Intensity (c/s)
10^6
10^5
10^4
10^3
10^2
10
1
0
25
50
75
Sputtering time (min)
Substrate →
← Substrate
29Si+
1H+
12C+



Intensity (a.u.)
× 75
−0.1
0.1
0.0
1.0
2.0
3.0
4.0
5.0
2θ (deg.)


Intensity (a.u.)
0.0
1.0
2.0
3.0
4.0
5.0
2θ (deg.)
−0.1
0.1


52
52
52
64
64
64
52
52
52
52
64
64
76
64
64
76
64
64
64
52
64
76
64