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Analysis of EXELFS modulations in EELS above the K-shell of silicon at 1 MeV in the HVEM

Raj Kumar Garg ⁽¹⁾, Alain Claverie ⁽²⁾ and Gérard Balossier ⁽³⁾

⁽¹⁾ Central Scientific Instrument Organisation, Sector-30, Chandigarh, 160020, India

⁽²⁾ Visiting Scientist at CSIO from Centre d'Elaboration des Matériaux et d'Etudes Structurales LOE/CNRS, 29 rue Jeanne Marvig, B.P. 4347, 31055 Toulouse Cedex, France

⁽³⁾ Laboratoire de Microscopie Electronique, UER Sciences, INSERM U 314, B.P. 347, 51062 Reims Cedex, France

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Résumé. — Des analyses EXELFS ont été réalisées sur différents films de silicium à 1 MeV dans des conditions rigoureuses. Nous avons observé que la présence de couches de contamination, telles que des oxydes ou des carbures de silicium, affectaient considérablement les oscillations EXELFS juste après le seuil K du silicium. La mise en évidence de la deuxième distance de coordination dans le silicium composé de plusieurs phases est beaucoup plus délicate, et la précision escomptée de $\pm 0.05 \text{ \AA}$ sur la mesure de la première distance n'est pas atteinte. Selon la gamme des valeurs des fréquences K retenues pour l'analyse, l'information structurale de la phase de plus faible concentration peut être révélée ou masquée. Enfin, nous montrons que pour des échantillons épais, nettoyés par une solution de HF, les résultats sont meilleurs à cause de la plus faible proportion d'oxydes. Dans ce cas, par ailleurs, les distances calculées pour les deux premières couches de coordination sont légèrement supérieures à celles attendues.

Abstract. — EXELFS experiments performed at 1 MeV in a high-voltage electron microscope (HVEM) under relatively straightforward conditions on several types of Si thin films have been analysed. It has been observed that the presence of a contamination layer, such as oxide or carbide, drastically affects the EXELFS oscillations past the Si K-edge. The visibility of the second neighbour distance of silicon is not clearly seen in specimens which are composed of several phases, and the expected accuracy of $\pm 0.05 \text{ \AA}$ in the first-neighbour distance is not reached. Depending on the K -range chosen for analysis, the structural information arising from the weakly present phase can be enhanced or removed. Finally, we show that the thicker specimens after HF cleaning give best results because of the small relative amount of oxide. In that case, however, the calculated distances for the first two distances are slightly higher than expected.

1. Introduction.

The Extended Electron Energy Loss Fine Structure (EXELFS) which occurs in the region up to several hundred eV above a core edge can be analysed in the same way as Extended X-ray Absorption Fine Structure (EXAFS) by using the formula of Sayers, Stern and Lytle [1] and

both techniques have been shown to yield information about the local environment around a selected atom [2]. The EXELFS technique in Electron Energy Loss Spectroscopy (EELS) has one significant advantage over conventional EXAFS ; it can be applied to microscopic areas of thin samples while EXAFS is likely to average structural informations over a large area of the material under probing. Since EXELFS can be carried out in the electron microscope, a sample can be analyzed by diffraction, conventional TEM and even high-resolution electron microscopy at the same time. It is expected to be a powerful tool when the material under investigation is not homogeneous at the microscopic scale from a structural or chemical point of view. Moreover, EXELFS appears as a useful probe for amorphous materials where alternative techniques can not give structural information (with perhaps the exception of computer-assisted electron diffraction, but then preferably in thin films containing a single element [3]).

Amorphous-like or poorly crystalline materials have received increasing attention during the last few years because of their various applications ranging from solar cell technology to metallurgy. In spite of this, only little information has been gained on the local atomic arrangement, the so called short-range-order (SRO) within these materials. The EXELFS technique offers a good spatial resolution which is of considerable importance in the case of non-homogeneous material such as matrix/fibre compounds or iron implanted semiconductors.

As our long-term goal is the characterization of ion-implanted amorphous semiconductors in relation to the mechanisms involved in the crystalline to amorphous phase transformation [4, 5], we have planned as a first step experiments on crystalline silicon thin films to see if we could obtain from a Fourier analysis of the EXELFS modulations the well-known first and second nearest-neighbour distances. The aim of this work is to study the influence of certain parameters used in the analysis, including those involved in data extraction and windowing of the K -range, on the final results. Special emphasis is placed upon the influence of contamination layers like carbon or oxide which are unavoidable when working with thin films. Various ion-milling, chemical-etching and vapour-deposition techniques were used during specimen preparation in order to provide different types of sample having different thicknesses of oxide on both sides. Several areas of the samples were analyzed then, careful EXELFS analysis were carried out and tested before correlating the results to the thickness of the contamination layer. For the sake of clarity, we have only returned in this paper some selected examples which however, are representative of the numerous experiments and analysis we performed. Incidentally, this has led us to study the influence of some carbon films intentionally evaporated on both sides of silicon. More generally, we discuss the effect of the presence of two distinct materials (i.e. some mixture) on the determination of the nearest-neighbour distances of silicon. Vanishing oscillations and low confidence in the choice of the threshold energy lead to a loss of accuracy in distance determinations. We will finally give, as a rule of thumb and for the used of experimentalists, some pre-requisite conditions on both specimen preparation and analysis procedure to attain the value of the first and second neighbour distances with some confidence. At least, it is expected that under similar conditions further experiments on amorphous or poorly crystallized silicon will give some new quantitative results which can be compared to the well-known crystalline material.

2. Experimental details.

2.1 SET-UP. — To observe EXELFS modulations in the electron energy loss spectrum, we have used a high-voltage electron microscope working most of the time at 1 MeV. This microscope is equipped with an Omega filter type electron spectrometer [6, 7]. The routine resolution is 3 eV at 1.2 MeV. However, for recording EXELFS modulations an energy resolution ranging from 5 to 10 eV has been used to increase the counting rate and hence to reduce the noise level. Further-

more, a 90° deflection prism is added underneath the microscope to protect the counting system from X-rays and from stray electrons produced by the incident electron beam along its path in the microscope column [8]. The photomultiplier output signal is electronically recorded in a computer and can be processed. The area of the sample that is analysed is limited by the selecting aperture in the intermediate lens. The magnification factor of the objective lens is about 60 so that the spatial resolution depends upon the size of the aperture but is currently in the micrometer range.

As the EXELFS modulations above the inner shells consist of small intensity fluctuations ranging in amplitude of a few percent (10 % near the threshold to 1 % at a few 100 eV above the edge), the signal-to-noise ratio for the detection of these modulations needs to be lower than 1 % . This corresponds to a counting rate larger than 10^4 per channel. Owing to the very low value of the inner-shell excitation cross-section at high voltages, such a high counting rate needs optimized instrumentation. Higher recording times can be a solution but at the cost of an increase in radiation effects ; this must be absolutely avoided in the study of amorphous semiconductors since it is known that high-energy electron irradiation can lead to recrystallization of these layers [9]. Another solution is to sacrifice the spatial resolution by using a larger selecting aperture but this is not always possible for non-homogeneous materials.

2.2 ADVANTAGE OF HIGH VOLTAGES. — A major problem in using electron microscopy for this type of study is related to the thickness of the samples. The thickness which produces the best visibility of the modulations is estimated to be such that $t/\lambda_p \leq 0.3$ where t is the specimen thickness and λ_p is the bulk or volume plasmon mean free-path [10]. It means that if $t = 500 \text{ \AA}$ at 1 MeV then it is 150 \AA at 100 keV, as the accelerating voltage dependence is introduced through λ_p which represents the main inelastic scattering process in the sample and there are no significant variations in it above 500 keV due to relativistic effects. Therefore, due to the variations of λ_p up to 500 keV, the new medium-high-voltage electron microscopes seem to provide very good conditions for the development of this technique. Most of the time we made experiments from an area in the image where the second plasmon peak was hardly visible or not visible at all [11]. More details on this aspect can be found in the review papers by Jouffrey *et al.* [12] and by Sevely *et al.* [13].

2.3 DATA ANALYSIS. — In this paper, analysis of EXELFS modulations past the silicon K-edge has been performed. Extraction of these modulations is carried out by subtracting to the spectrum some polynomial function which fits to the average intensity after the edge. This polynomial fitting is the most crucial step for obtaining a high accuracy ($\pm 0.05 \text{ \AA}$) for the first and second nearest neighbour distances around some chosen central atom. In most of the cases, the K -range of the ejected electron wave is limited in EXELFS from 3.5 to less than 10 \AA^{-1} , smaller than EXAFS for which K ranges up to 15 \AA^{-1} . For this reason a simple polynomial fitting program [14] works well to extract EXELFS modulations from the available limited K -range, and determination of the first and second nearest-neighbour distances can be interpreted with a high degree of confidence. However, it may be possible to obtain atomic distances beyond the second shell with some accuracy (to be useful like a fingerprint) if a more rigorous method is employed to extract the EXELFS modulations, because the maximum K -range can then be used with confidence provided adequate signal-to-noise ratio is present in the recorded spectrum.

An important aspect of EXELFS data analysis is the choice of the zero of the K -scale. An error in the choice in the threshold energy of $\Delta E_0 = 10 \text{ eV}$ produces a shift of about 0.1 \AA for a first-neighbour distance if situated at 2 \AA . Therefore, to find the correct $K = 0$ position, it is more accurate to treat E_0 as a free parameter adjusting it through the criterion of Lee and Beni

[15] which states that owing to the sine dependence of $X(K)$ versus K , the magnitude and the imaginary part of the Fourier transform should peak at the same value of R . For this reason, use of the inflection point (half height of the edge) of the inner shell as a choice of $K = 0$ position must be rejected.

Windowing of the K -range is also of major importance since complete oscillations must be present after windowing with no step-like variations at the edges : a "good" K -range should start and end at modulation nodes. This, however, can easily be detected in the Fourier transform through the presence of a large peak centred at the $R = 0$ position. In any case, to avoid some undesirable steps in the vicinity of the nodes, the usual rectangular window was smoothed by a gaussian shape, affecting the beginning and end of the window over about 5 eV. In all our analyses, many runs were performed to minimize this $R = 0$ peak. Optimization of the polynomial fitting leads, after extraction, to well-balanced $X(E)$, and then, $K \cdot X(K)$, oscillations.

3. Results.

3.1 VAPOUR-DEPOSITED SILICON. — An example of a raw spectrum is given in figure 1a where the Si K edge is recorded. This specimen, about 500 Å thick, was a silicon film prepared by electron beam evaporation onto a NaCl substrate. It was rinsed in deionized water and then quickly loaded in the electron microscope. The oxide thickness was then supposed to be less than is usual with some standard preparation technique such as ion-milling. The experimental parameters of the recording as well as the analysis are given in the associated captions. In spite of some noise in the spectrum due to the low count level in this experiment, well-balanced oscillations can be obtained after data smoothing and extraction by polynomial subtraction. The low counting rate is due to the small size of the aperture in front of the photomultiplier tube of the detector system as well as to the restricted area under analysis. This helped to reduce the entry of spurious X-rays and electrons. Moreover, in our earlier experiments the beam current was kept comparatively low to avoid aperture drift, as the recording time of 10 minutes was quite large. Later on, these conditions were optimized to increase the count rates as is evident from the other spectra. The extracted $K \cdot X(K)$ function is plotted in figure 1b through its window ranging from 3.75 to 9.37 Å⁻¹. This signal which is to be Fourier transformed is well-balanced and the cut-off frequencies are situated near oscillation nodes. The Fourier transform is shown in figure 1c, giving evidence for two first shells at 2.1 and 3.55 Å respectively. The dotted line depicts the imaginary part while the full line gives the amplitude of the Fourier transform. The first two peaks are nicely matched, which is an indication of an acceptable choice of the threshold energy. They are clearly stronger than other peaks beyond the second shell, perhaps due to the noise.

This example is representative of most of the analyses we have currently performed on silicon thin films ; two distinct shells are generally observed as long as a careful analysis is performed and the specimen is not heavily contaminated. However, as a rule of thumb, the calculated distances are somewhat higher than expected. It is known, since the theoretical calculations of Teo and Lee [16], that owing to a phase shift problem in the vicinity of both the central as well as the scattering atoms, corrections must be made to the calculated values. This is represented in figure 2 where we have plotted the total phase-shift correction for the Si-Si pair as given from theoretical calculations [16] as well as linear approximations which can be used depending on the available K -range. The linear assumption can be made and the phase-shift correction is obtained after Fourier transformation by adding one half of the slope of the linear approximation. In the case of silicon it is shown that, if experimental spectra are recorded over a large K -range varying from 3.7 to 15 Å⁻¹ (as can be the case for EXAFS), a correction of about 0.33 Å must be added to the

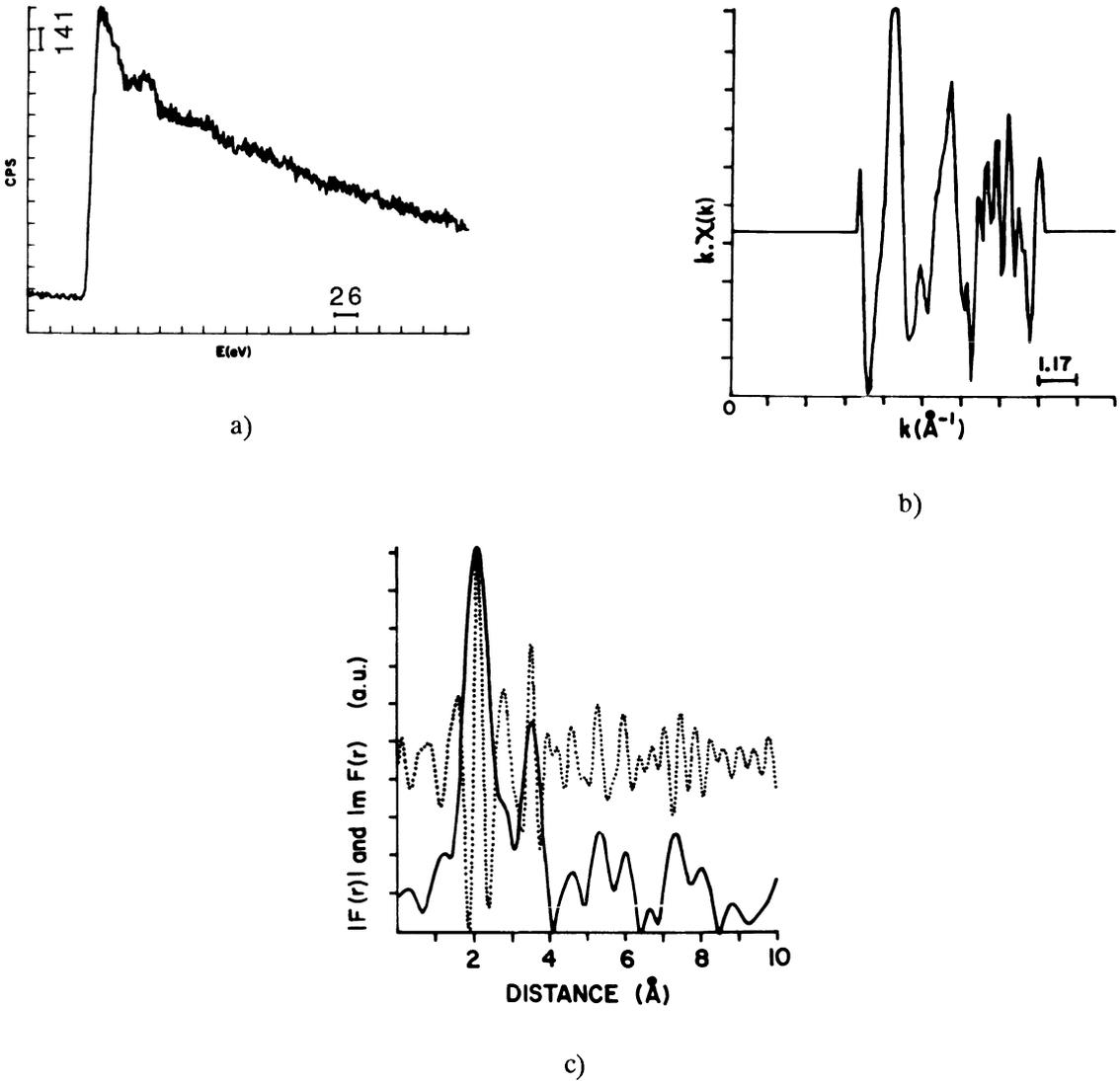


Fig. 1. — Vapour-deposited silicon. (a) EXELFS modulations past the Si K-shell at 1839 eV. Experimental parameters are : accelerating voltage $V_0 = 1$ MeV, energy resolution of the spectrometer $E_R = 5$ to 10 eV, recording time $T = 0.3$ s channel, semi-angle of the spectrometer $\alpha = 0.003$ rad, diameter of the analyzed area $d = 1.67 \mu\text{m}$, energy increment per channel $\Delta = 1.0763$ eV. (b) EXELFS oscillations $K \cdot X(K)$ versus $K (\text{\AA}^{-1})$ above the Si K-shell as shown in figure 1a. The data are shown only in the region 3.75 - 9.37\AA^{-1} . The zero of the K-scale corresponds to -22 eV below the inflection point (i.e. half height of the edge). (c) Magnitude and imaginary part of the FFT of $K \cdot X(K)$ data of figure 1b. The first and second nearest neighbour distances without correction due to phase shifts are 2.10\AA and 3.55\AA respectively.

calculated value as confirmed by experiments [17]. If the K -range is limited from 3.5 to 8\AA^{-1} , which is usual for EXELFS, one may expect the correction to be about 0.46\AA . Considering now our experimental results, only a correction of only about 0.25 - 0.3\AA can give us the known first distances of silicon at 2.35 and 3.84\AA .

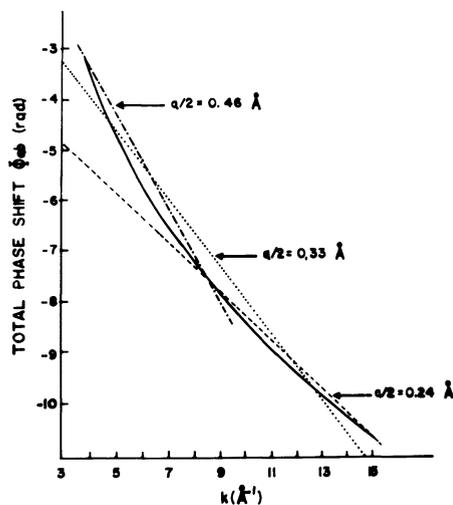


Fig. 2. — The solid curve represents the total phase shift for Si-Si pair as calculated by Teo and Lee [16]. Assuming that the phase shift is approximately linear in K over the EXELFS energy range with a negative slope i.e. $\phi = -aK + b$, a correction of “ $a/2$ ” has been shown in three domains of K -range. The average value of $a/2 = 0.35 \text{ \AA}$ may be used as a correction value.

Silicon is chemically a very active material especially under oxygen or carbon exposure in air as well as under the high vacuum available in the electron microscope. Oxidation on both sides of the thin films occurs within a short time and this can even lead to the formation of layers of several tenths of Angströms depending on surface roughness and crystallinity [18]. For rough specimen (for example after ion-milling) and waiting for a few days or weeks before performing the experiment, these layers can reach a thickness of nearly 100 Å. For EXELFS analysis a “good” specimen thickness is of about 500 Å so that these oxide layers are able to contribute in the worst cases as much as 20 % of the observed EXELFS modulations. This type of problem is likely to occur as soon as one is dealing with any sample consisting of a mixture of a single element plus its own oxide, for example. It should not be considered as arising from random noise which can be filtered out in the course of data processing. Since a central Si atom can be surrounded by others Si atoms in the case of pure silicon, or by oxygen atoms in the case of the oxide layers, the EXELFS modulations after the Si-K edge consist of the addition of two types of oscillations which are difficult to separate. Therefore, it is expected that in the case of any mixture the choice of the threshold energy which fix the origin of the wavevector K is different. For example, silicon and silicon oxide, because of the insulating properties of the later, have a different K origin. As a first step and in order to check the influence of an extra-layer on the EXELFS analysis, further experiments were carried out on carbon coated-silicon specimen.

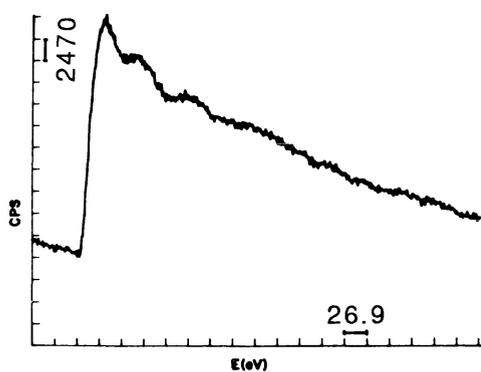
3.2 CARBON-COATED SPECIMENS. — These specimens were thermally evaporated, 500 Å thick polycrystalline silicon. Before and after evaporation of the Si film a deposition of about 50 Å of carbon was carried out under the same vacuum to provide a coating on each side of the sample. The EXELFS experiments were carried out on a fresh specimen ; the recorded spectrum is shown in figure 3a. Figure 3b shows the $X(E)$ oscillations after extraction in the $3.5\text{-}8 \text{ \AA}^{-1}$ range ; it exhibits nearly three complete oscillations. Figure 3c shows the magnitude and the imaginary

part of the Fourier transform of $K \cdot X(K)$ as calculated from figure 3b. It is noticeable that both curves exhibit only one strong peak, no distinct features being distinguished over the almost flat curve extending to larger R values. The matching of the magnitude and the imaginary part is good but once more we notice that, without any phase-shift correction, the first-neighbour distance is given at 2.16 Å, at least 0.16 Å higher than expected for pure silicon. A new analysis was performed on the same spectrum but extending the K -range as far as possible i.e. up to 11 Å. The result is shown in figure 3d. In spite of some noise, several extra peaks can be resolved over large distances. Keeping in mind that these peaks must be treated with low confidence, it is interesting to note that they occur at distances expected for silicon and silicon carbide. Thus it is supposed that the EXELFS modulations carry information both in silicon itself and also on the carbide layer formed after reaction of carbon on the silicon surface.

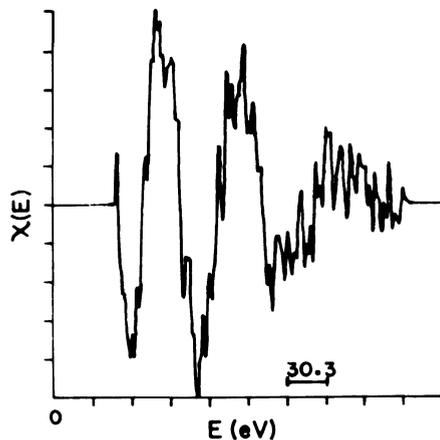
In all experiments of this type that we have investigated, the general trends were as follows : The effect of a mixture of carbon and silicon increases the calculated distances by about 0.15 Å and, in addition, when noise is important or the K -range sharply limited, only one peak giving an inaccurate first-neighbour distance can be clearly resolved. It is deduced that the EXELFS modulations from the pure silicon are spoiled by a carbide contribution in the spectrum. When high signal-to-noise ratios offer the possibility of extending the K -range to greater values, new features appear in the amplitude of the Fourier transform which may be assigned to silicon carbide. Note also that the threshold energy is far from the inflection point (-17 eV) of the K-edge, but the jump at the edge is less abrupt than for the pure silicon. Since there is no reason for the threshold energies to have the same value in silicon and silicon carbide, matching of all the shells appearing in the FT cannot be done properly. As an experimental result, we see that it leads to somewhat lower threshold energies than given in the literature for EXAFS.

3.3 ION-MILLED SILICON SPECIMENS. — Some specimen were prepared by a method normally used for cross-sectional electron microscopy observations [14]. Thin silicon “sandwiches” were cut, mechanically thinned and polished, and then submitted to Ar⁺ sputtering at 5 keV until a small hole was made. It is well-known that under these conditions of preparation, the thin films are covered with an amorphous layer on both sides and moreover the roughness of the film is very high. On this type of specimen, oxidation is likely to occur with high efficiency especially when exposed to air and EELS experiments indicated the presence of oxide through the oxygen K-edge visible in the spectrum. Figure 4a shows the spectrum obtained for the Si K-edge on the same specimen while a first analysis is shown in figure 4b for a K -range ranging from 3.8 to 7.5 Å⁻¹. It is clear that only one peak is visible in the magnitude of the FT and that no extra features can be distinguished. One other troublesome result is that, satisfying the criterion of Lee and Beni [15] (i.e. matching the peaks of magnitude and imaginary part) leads to a threshold energy value of -31 eV which is much greater than expected for silicon. Again the calculated distance at 2.1 Å is too high without any phase-shift correction. Finally, the same analysis was performed but extending the K -range from 3.5 to 9.1 Å⁻¹; the result is shown in figure 4c. Note that in this case the second-neighbour distance of silicon is not resolved while the first shell at 1.2 Å may be related to a Si-O distance due to the oxide. In any case, on matching the magnitude and imaginary part of the first shell of silicon, the Si-O shell could not be matched properly and vice-versa. Again, the mixture of two distinct materials having the same central atom leads to some confusion in the choice of the $K = 0$ position.

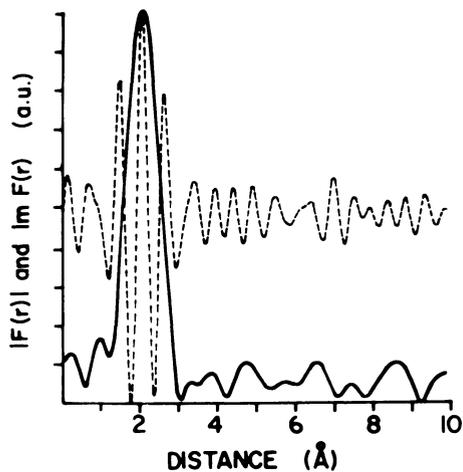
The same specimen was extracted from the microscope column, cleaned in a HF solution to remove the oxide, rinsed in deionized water and then quickly reloaded for analysis. New spectra were recorded under similar conditions; one of them is shown in figure 5a. Note that the jump at the edge appears sharper than previously reported and that the oscillations seem to be enhanced



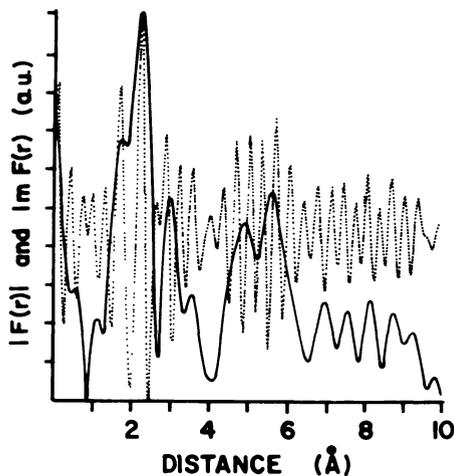
a)



b)



c)



d)

Fig. 3. — Carbon-coated silicon. (a) EXELFS modulations past the Si K-shell. Experimental parameters are : $V_0 = 1$ MV, $E_R \cong 5$ to 10 eV, $T = 0.3$ s channel, $\alpha = 0.003$ rad, $d = 1.67$ μm , $\Delta E = 1.0763$ eV. (b) EXELFS oscillations $X(E)$ versus energy E above the Si K-shell according to figure 3a. The data are shown only in the region 45 eV (3.45 \AA^{-1}) to 276 eV (8.51 \AA^{-1}). The zero of the E -scale or K -scale corresponds to -23 eV below the inflection point. (c) Magnitude and imaginary part of the FFT of $K X(K)$ data of figure 2b. The first nearest neighbour distance without correction due to phase shifts is at 2.16 \AA . Note that the second nearest neighbour peak is not visible. (d) Magnitude and imaginary part of the FFT of $K X(K)$ data of figure 2a in the region 4.2 - 10.87 \AA . The zero of the K -scale is 17 eV below the inflection point. The first, second and third nearest neighbour distances without correction due to phase shifts are at 1.70 \AA , 2.20 \AA and 3.00 \AA respectively. The large peaks at 4.90 \AA and 5.6 \AA indicate several unresolved shells and would depend on the relative amount of their contribution (which again depend on the K -domain used for analysis).

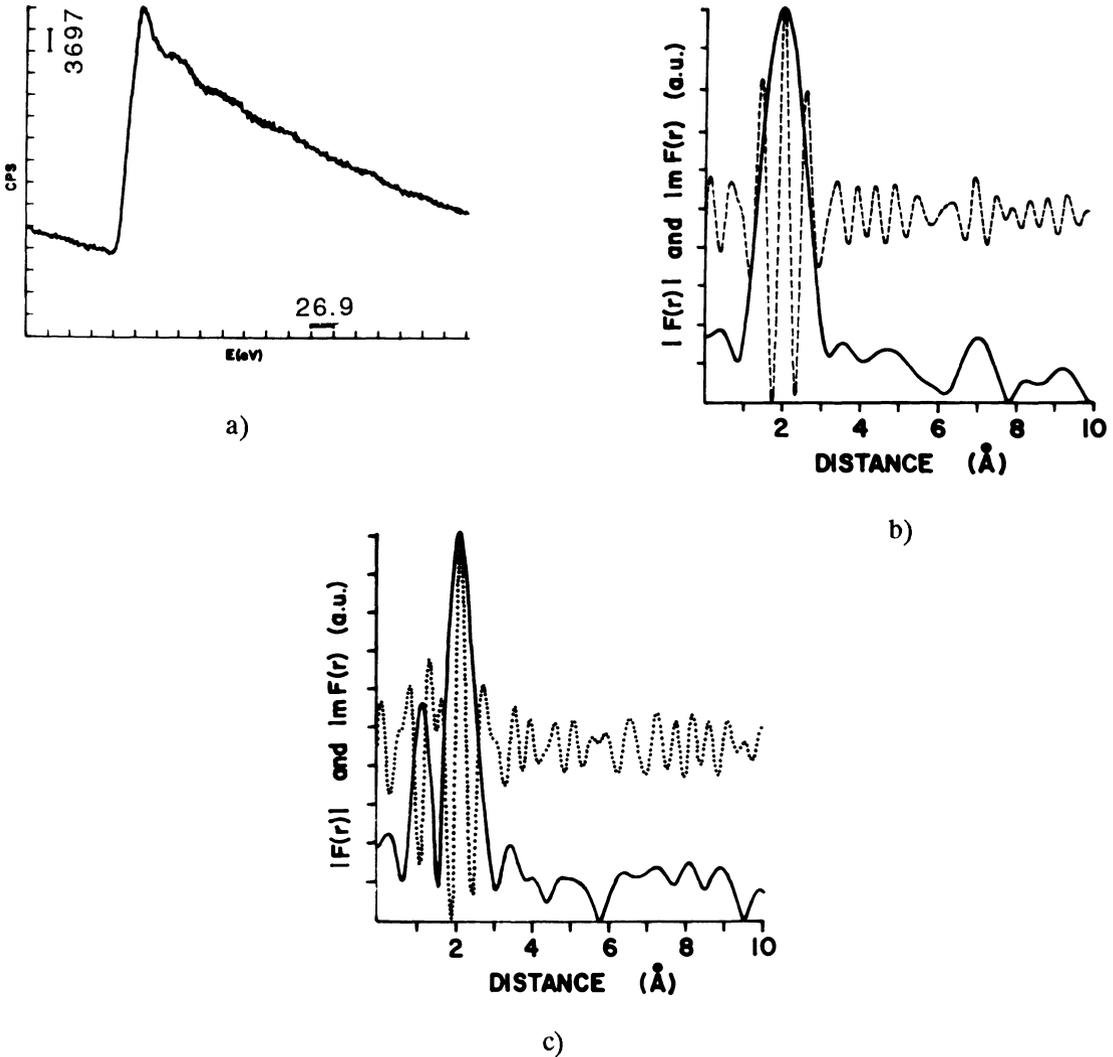


Fig. 4. — Ion-milled silicon. (a) EXELFS modulations past the Si K-shell. Experimental parameters are : $V_0 = 1$ MV, $E_R \cong 5$ to 10 eV, $T = 0.3$ s/channel, $\alpha = 0.003$ rad. $d = 0.5 \mu\text{m}$, $\Delta E = 1.0763$ eV. (b) Magnitude and imaginary part of the FFT of $K X(K)$ data of figure 4a in the region of $3.8 - 7.50 \text{ \AA}^{-1}$. The zero of the K -scale is -31 eV below the inflection point. The first nearest neighbour distance without correction due to phase shifts is at 2.09 \AA . Note that the second-neighbour peak (for Si-Si) is not clearly visible. (c) Magnitude and imaginary part of the FFT of $K X(K)$ data of figure 4a but in the region $3.49 - 9.06 \text{ \AA}^{-1}$. In this case the zero of the K -scale is -18 eV below the inflection point. The first and second-neighbour distances without correction due to phase shifts are at 1.18 \AA and 2.12 \AA respectively. Again the 2nd-peak for Si-Si pairs in Si is not clearly visible. However, the first peak is due to Si-O pairs of SiO_2 phase but the magnitude and imaginary parts are not matching.

with respect to the same sample before cleaning. Analysis of this spectrum was carried out for a K -window extending from 3.5 to 7.5 \AA^{-1} (Fig. 5b). It is clear that two strong peaks are present in the magnitude of the FT and can be accurately matched with the imaginary part. In this case

the "oxide" peak is missing and the calculated distances without any phase correction are 2.17 and 3.65 Å respectively. To account for the well known distances of silicon, a phase correction of about 0.2 Å is required, which is again less than expected. In any case, this specimen is not assumed not to be oxide free, which is not possible under ordinary vacuum conditions as well as after transfer into the air, but the thickness of the oxide layer is far less than before HF cleaning as confirmed by EELS analysis.

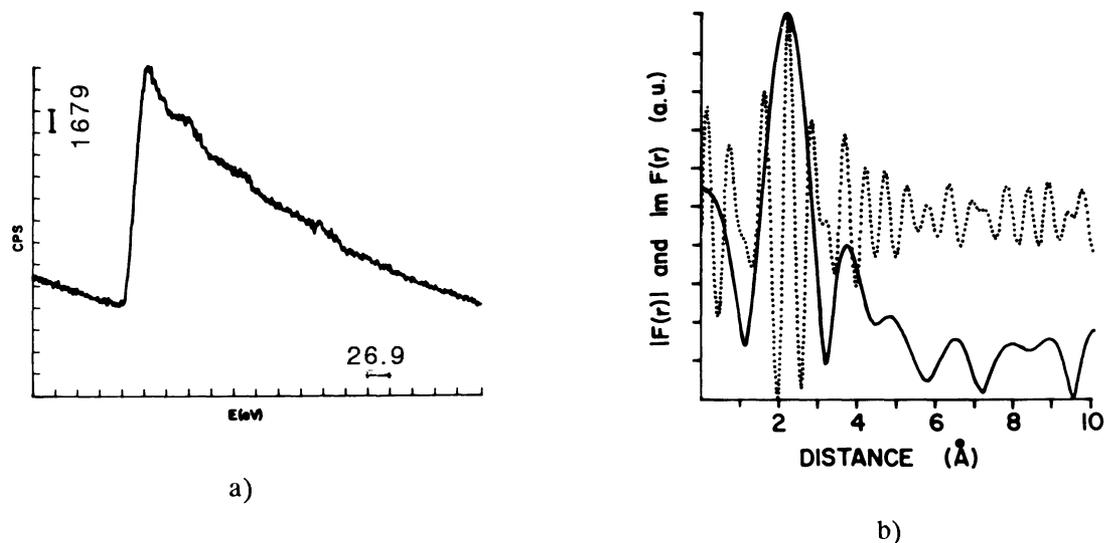


Fig. 5. — (a) Ion-milled silicon. EXELFS modulations past the Si K-shell. Experimental parameters are : $V_0 = 1$ MV, $E_R \cong 5$ to 10 eV, $T = 0.4$ s/channel, $\alpha = 0.003$ rad, $d = 0.5$ μm , $\Delta E = 1.0763$ eV. (b) Ion-milled silicon after HF cleaning. Magnitude and imaginary part of the FFT of $K \cdot X(K)$ data of figure 4a in the region of $3.45 - 7.49$ \AA^{-1} . The zero of the K -scale is -20 eV below the inflection point. The first and second-distances without correction due to phase shifts are at 2.17 Å and 3.65 Å respectively. The peak due to Si-O pairs of SiO_2 phase is missing.

As a conclusion, it is noted that when the specimen is heavily oxidized, only one first shell can be resolved in the magnitude of the FT while extending the K -range results in the appearance of some extra features that can be related to the oxide layer. Moreover, the threshold energy is seen to be less for pure silicon than that for the heavily oxidized material. After cleaning, the first and second neighbour distances of silicon can be obtained with some accuracy, in spite of the need for a smaller distance correction than expected according to theory. While not fully understood, this effect seems to arise from the presence of a little oxide on both sides of the specimen, perturbing the balance of the modulations representative of both phases and hence the position of the threshold value.

3.4 THICKER SPECIMENS. — One other possibility for minimizing the effect of the oxide layer is to increase the amount of silicon material i.e. to work on thicker specimens. Figure 6a shows a spectrum recorded on an approximately 700 Å thick chemically-etched silicon specimen. Increasing the thickness results in an increase of counts per channel while the visibility of the EXELFS modulation over a large energy range is improved. Two distinct analyses have been performed on this spectrum. In the first (Fig. 6b) the K -window extends from 5.2 to 11.7 \AA^{-1} ; two shells

are seen at 1.34 and 2.17 Å and give the distances for Si-O and Si-Si respectively. The second-neighbour distance of silicon (at 3.84 Å) is missing or not resolved from the background. When analysing the same spectrum but in a more limited K -range starting on the first EXELFS oscillation at 3.5 \AA^{-1} , we obtain the result shown in figure 6c. In this case, the peak at about 1.2-1.3 Å is no more visible while the second neighbour distance of silicon is given at 3.67 Å without any phase-shift correction.

We note that increasing the thickness of the specimen results in better visibility of the first two neighbour distances of silicon if one does not extend the K -window too much. Again, we see that the calculated distances are slightly higher than expected.

Conclusions.

Several types of silicon thin films were prepared : for example, e-beam evaporated on rock salt, chemically-etched, ion-milled and carbon-coated films. In order to study the local atomic order in these films, EXELFS experiments were performed under relatively straightforward conditions. After careful analysis of the EXELFS modulations, the following general trends have been observed.

(i) As expected, the presence of native silicon oxide and a SiC phase on carbon-coated films can be seen. The first peak in figures 4c and 6b seems to correspond to a Si-O pair in the SiO₂ phase, whereas the first peak in figure 3d may correspond to a Si-C pair in the SiC phase.

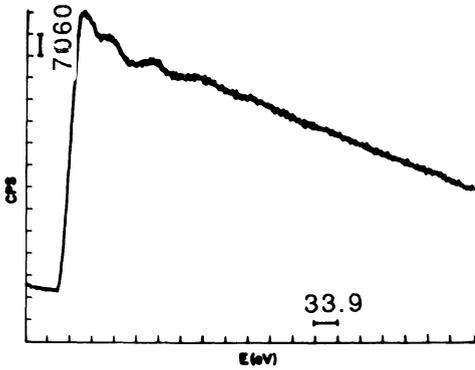
(ii) On the basis of the present analysis, it is much easier to observe the oxide or carbide phase when the K -window is chosen with K_{\min} such that the first negative oscillation is ignored and K_{\max} is a maximum consistent with an acceptable noise level (i.e. the modulations must be visible at least by eye). The large K_{\min} value reduces the influence of the dominant phase in the specimen.

(iii) The visibility of the second-neighbour distance corresponding to the dominant phase of the specimen is not clearly seen in specimens which are composed of several phases. Moreover, the expected accuracy ($\pm 0.05 \text{ \AA}$) in the first-neighbour distance is also not obtained. It is 0.1 to 0.2 Å larger, perhaps due to the large negative value ($\cong -20 \text{ eV}$) of the threshold energy (i.e. $K = 0$ position) before the inflection point.

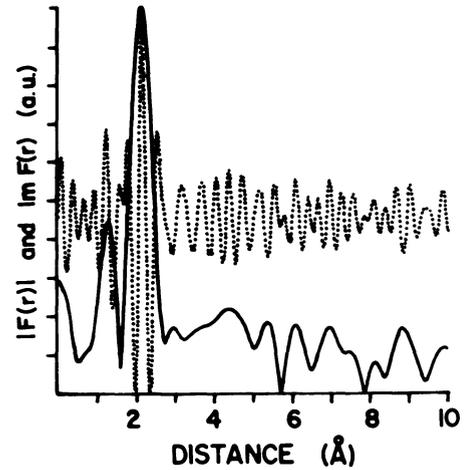
(iv) Analysis of the small K -range ($\leq 8 \text{ \AA}^{-1}$) with K_{\min} as small as possible provides the following information. The first peak, corresponding to the oxide or carbide phase, disappears. The second peak, corresponding to the first-neighbour distance of the dominant phase is, of course, present but is larger by 0.1 to 0.2 Å. The third peak corresponding to the second-neighbour distance of the dominant phase is not visible at all when the weakly present phase is more than 10-20 %. When it is less, then the second-neighbour peak is visible but once again the accuracy is very poor as for the first-neighbour distance.

We propose the following new criterion for a quick analysis of the specimen with mixed phases. The visibility of the second-neighbour distance corresponding to the dominant phase is a good guide to estimate any interference of a weakly present phase. However, if the first and second peaks are well within expected accuracy ($\pm 0.05 \text{ \AA}$), then the specimen may be considered relatively free from contamination. In such cases, the relative height of the second-neighbour peak might be a good criterion to estimate the level of crystallinity of the specimen. Thus, the relatively thicker specimens and the use of HVEM for EXELFS experiments are advantageous to minimize the interference of weakly present phases in the specimen (e.g. see the analysis of Fig. 6a).

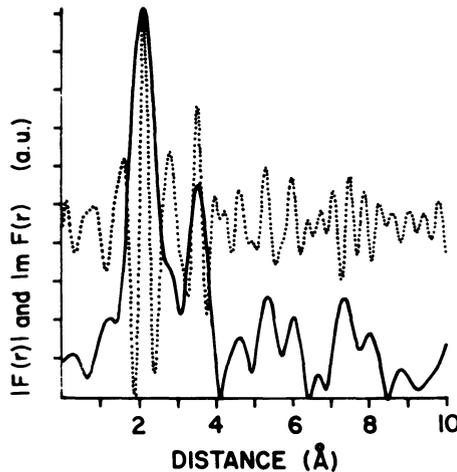
More generally, we believe that the new medium-high-voltage associated with a parallel detection system provides good conditions for the development of the EXELFS technique but that



a)



b)



c)

Fig. 6. — 700 Å thick chemically-etched silicon. (a) EXELFS modulations past the Si K-shell. Experimental parameters are : $V_0 = 1$ MV, $E_R \cong 5$ to 10 eV, $T = 0.28$ s/channel, $\alpha = 0.0018$ rad, $d = 0.5$ μ m, $\Delta E = 0.72$ eV. (b) Magnitude and imaginary part of the FFT of $K^2 \cdot X(K)$ data of figure 6a in the region of $5.24 - 11.66 \text{ \AA}^{-1}$. The zero of the K -scale is -21 eV below the inflection point. The first and second-distances without correction due to phase shifts are at 1.34 \AA and 2.17 \AA respectively. The first peak is due to Si-O pairs of SiO_2 phase but its /FFT/ and $\text{Im}/\text{FFT}/$ parts are not matching. The second shell peak of Si-Si pair in silicon is not visible. (c) Magnitude and imaginary part of the FFT of $K \cdot X(K)$ of figure 5a but in the region from 3.53 to 7.27 \AA^{-1} . The zero of the K -scale is -17 eV below the inflection point. The first and second-distances without correction due to phase shifts are at 2.20 \AA and 3.67 \AA respectively. The peak due to Si-O pairs of SiO_2 phase is missing.

quantitative analysis will be possible only if the material under investigation is free from any contamination layer i.e. the specimen shall be prepared and transferred in the column under nearly Ultra-High-Vacuum conditions. Under the present experimental conditions however, it is concluded that EXELFS may be applied to the study of amorphous or "disordered" silicon provided one restricts the study to a comparative work on the same clean specimen with no thickness variations from one area to the other.

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