

CRYSTAL-AMORPHOUS PHASE TRANSITION INDUCED BY BALL-MILLING IN SILICON

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Summary

We present an experimental study of the first reported crystal-amorphous phase transition induced by ball-milling in a pure element: a silicon powder. Scanning electron microscope observations show some particular spherical particles with smooth shapes. Only minor contamination with iron and chromium (less than or equal to 0.2 at.%) has been determined by chemical EDX microanalyses. The analyses of the X-ray patterns reveal the coexistence of silicon microcrystallites and an amorphous phase. Transmission electron microscope investigations (selected area diffraction patterns) show that such mixing is on the micrometer scale. The various enthalpic evolutions which have been studied by differential scanning calorimetry experiments reveal three major contributions which may be successively interpreted starting from room temperature up to 725 °C as a release of the strain energy (exothermic event), followed by an equilibration between the *in situ* differential scanning calorimetry annealed silicon crystallites and the amorphous phase (endothermic effect), and subsequently by the crystallization of the amorphous phase (exothermic contribution). The influence of the ball-milling conditions on the dynamic equilibrium between the crystalline and the amorphous phases has been studied.

1. Introduction

Amorphous phase formation by mechanical alloying was first reported by Yermakov *et al.* [1] and Koch *et al.* [2] for the Co-Y and Ni-Nb systems respectively. Subsequently, such an amorphization process has been observed in many other binary alloy systems, starting from elemental crystalline powders, *e.g.* Fe-Zr [3], Ni-Zr [4-6], Ti-Pd [7], Ni-Ti, Co-Ti, Fe-Ti [8-10], Ti-Cu [11], Co-Sn [12], or from a mixture of intermetallic compounds in the Ni-Zr system [13-15].

Amorphization by mechanical alloying is usually obtained in the case of binary alloys exhibiting a large negative heat of mixing and for which one of the elements is a fast diffuser [16]. Nevertheless, such an amorphiza-

tion has been observed by Richards *et al.* [17] in Cu–Ag alloys with a positive heat of mixing, as well as in a slow diffusing system $V_{29}Zr_{71}$ by Weeber *et al.* [18]. Amorphization of intermetallic compounds has been attributed to the free energy increase due to accumulation of point and lattice defects leading to the destabilization of the crystalline compounds [19].

Although such an argument holds for the crystalline–amorphous phase transition, it cannot apply to the elemental powder–amorphous phase transition for which amorphization is argued to result from the solid state interdiffusion reaction occurring at the clean and fresh interfaces between two elemental metal layers [20], as is the case for the classical solid state amorphization by diffusion between deposited multilayers [21]. Nevertheless, in some cases, starting from elemental powders, the formation of crystalline intermetallic compounds preceded the formation of amorphous phases [5, 6] or they may even coexist with the latter during the stationary ball-milling state [5, 6]. This is in contradiction to the investigations of the different steps of the so-called classical solid state amorphization process for which the appearance of the crystalline compounds stops the development of the amorphous phase and reduces the thickness of the latter by a recrystallization process.

Furthermore, Loeff *et al.* [22] report the decomposition of the binary alloys La–TM (TM $\equiv$ Ag, Ni, Co) into the elements in spite of the negative heat of mixing which exists in such systems.

In fact, the end product of the ball-milling process, namely a homogeneous amorphous phase, or a mixture of glass and crystalline compounds, or purely crystalline compounds seems to be highly dependent on the milling conditions: milling atmosphere, balls-to-powder weight ratio, balls and vial materials, type of ball movement and average milling temperature.

From our knowledge, up to now, ball-milling amorphization processes have been performed starting with a mixing of elements. In this paper, for the first time we report on the crystal–amorphous phase transition induced by ball-milling in a pure element: a silicon powder. The morphological, structural and thermal stability of the ball-milled powder have been investigated by means of scanning electron microscopy (SEM) equipped with EDX microanalyser, X-ray diffraction pattern, analysis transmission electron microscopy (TEM; selected area diffraction pattern) and differential scanning calorimetry (DSC).

2. Experimental details

2.1. Ball-milling conditions

Pure silicon (10g; Hyperpure Polycrystalline Silicon, Wacker Chemi-tronic, GmbH; 300 Ω cm n and 3000 Ω cm p) was introduced into a cylindrical tempered steel (12% Cr, 2% C) container of capacity 45 ml. This procedure was performed in a glove box filled with purified argon. Each

container was loaded with five steel balls (diameter, 1.5 cm; mass, 14 g). The containers were sealed in the glove box with a Teflon O-ring and the milling proceeded in stationary argon.

Ball milling was carried out using two Fritsch planetary high-energy ball-milling machines (Pulverisette P7/2 and P5/2). In the case of the latter machine, two intensity settings were chosen which are mentioned later as P5/2(10) and P5/2(5). The different ball-milling conditions will be referred to as Si(I), Si(II) and Si(III) for the P7/2, P5/2(10) and P5/2(5) conditions respectively. The higher energetic conditions correspond to Si(I), the lower ones relate to Si(III).

The durations of the continuous milling processes were 95 h, 70 h and 96 h for Si(I), Si(II) and Si(III) respectively.

2.2. SEM and chemical microanalyses

Some silicon particles were removed from the vial for further electron microscopy investigations: the particle morphology was characterized using a digital scanning electron microscope (Zeiss DSM 950) in the secondary electron image mode. In order to evaluate possible container contamination which may have occurred by friction of the particles on the balls and the walls of the container, EDX analyses with an electron probe diameter of about 1 μm (in fixed-mode spot analyses) or on large surfaces (in scanning mode) were performed using the Si-Li detector and the Tracor EDX analyser in conjunction with the scanning electron microscope. A semi-quantitative program with internal references (*SQ* from Tracor) was used to analyse the EDX spectra. The SEM conditions chosen for the chemical determination were: 20 kV for the high voltage and a take-off angle of about 50°.

2.3. X-ray investigations

After continuous milling, a small amount of ball-milled powder (0.3 - 0.6 g) was extracted from the container and glued onto a SiO_2 plate for X-ray investigation. The X-ray diffraction patterns of the silicon ball-milled powders were obtained using a (θ - 2θ) Philips diffractometer with $\text{Co K}\alpha$ radiation ($\lambda = 0.17889 \text{ nm}$).

A numerical method was used to analyse the X-ray diffraction patterns and to obtain the position and the full-width at half height (FWHH) of the various peaks. In the *ABFit* program [23], the spectrum is modelled by a polynomial background with a maximum degree of two plus a set of simple shaped peaks. Then the Y value of the pattern is:

$$Y(x) = \text{Bkg}(x) + \sum_{i=1}^n \text{peak}_i(x, S_i, I_i, X_i, L_i)$$

where i is the index of the n possible peaks, x is the Bragg angle in 2θ , $\text{Bkg}(x)$ is a polynomial with a degree of 0 to 2 defining the background $\text{Bkg}(x) = b_0 + b_1(x - x_m) + b_2(x - x_m)^2$, x_m is the abscissa of the centre of the $[\theta_{\min}, \theta_{\max}]$ angular domain of the observed pattern, S_i is a peak shape

parameter allowing the selection of the appropriate function and I_i , X_i , L_i represent the intensity, position and FWHH of the i th peak.

The functions which describe the peaks have been reparameterized in the *ABFfit* program as a function of the integrated intensity (I), the mean position of the peak (μ) and the FWHH (L) are of three kinds:

gaussian curve:
$$\left\{ \frac{Ib}{(2\pi L^2)^{-1/2}} \right\} \exp \left\{ -\frac{b^2(x - \mu)^2}{2L^2} \right\}$$

with $b = 2(2 \ln 2)^{1/2}$ and $L = \sigma b$

modified Lorentz curve:
$$\frac{2bIL^3}{[\pi\{L^2 + b^2(x - \mu)^2\}^2]}$$

with $b = 2\{(2)^{1/2} - 1\}$ and $L = ba^{-1/2}$

Cauchy curve:
$$\frac{2IL}{[\pi\{L^2 + 4(x - \mu)^2\}]}$$

with $L = 2a^{-1/2}$

where σ^2 is the variance of the gaussian function and a is a parameter of the Cauchy or the Lorentz functions.

For the determination of the proper end-fit, we have adopted the following criteria:

(i) The root mean square deviation of the integrated intensity of a given peak has to be less than the value of the integrated intensity.

(ii) As the *ABFfit* program works on a limited number of angular values, we have been obliged to partition all the angular domains into two successive angular domains (*i.e.* $25^\circ - 50^\circ$ and $45^\circ - 75^\circ$ in 2θ), the choice of the mean particle sizes has to be the same in the deconvolution of the two angular domains, *i.e.* one amorphous phase plus one size of crystalline grains, or one amorphous phase plus two sizes of particles.

Bragg's expression has been applied to determine the d parameter corresponding to the diffraction peak position (θ):

$$\lambda = 2d \sin \theta$$

The effective diameter of the particles (hereafter referred as Φ) has been calculated from the Scherrer's expression:

$$\Phi = \frac{0.91\lambda}{(B \cos \theta)}$$

where λ is the X-ray wavelength, B the linewidth and θ the diffraction angle.

2.4. TEM investigations

Some silicon particles were spread on copper TEM grids in order to study the microstructural state using a Jeol 2000FX transmission electron microscope. The structural state was investigated by selected area diffraction patterns which were obtained on the edges of the silicon particles and/or on some particles which were thin enough to be observed and which remained

on the edge of the copper grid. No electrochemical polishing or ionic pulverization was used to obtain thin foils. Therefore, no structural artefact could have been introduced by such classical foil preparation techniques.

2.5. Calorimetric measurements

The thermal analysis was carried out using a DSC - 2C (Perkin-Elmer) with various heating rates β ranging from 2.5 to 40 °C min⁻¹. A sample of 20 mg was sealed in a copper capsule and heated from 50 to 725 °C under flowing pure argon. Several successive runs were applied to the same sample until the DSC curves were reproducible for two successive runs. The last curve was considered as the reference baseline which was then subtracted from all of the preceding curves. In this way the effective effect was shown. Indeed, this subtraction removes the drift of the baseline which is a feature of the calorimeter: even if the baseline is adjustable, a perfect straight line is never observed. It is S-shaped and must be readjusted for each chosen heating rate. Thus the subtraction of the apparatus drift contribution unambiguously reveals the endothermal and exothermal phenomena occurring on heating, by comparison (difference) with the final well-defined high-temperature annealed specimen. Nevertheless, if the latter undergoes some reversible phenomena on heating, such a method is not able to show it.

3. Results

3.1. SEM

Figure 1 shows typical scanning electron micrographs of silicon powders. Two kinds of particles can be distinguished: some exhibit a particular spherical shape, with smooth curvature and no asperities (Fig. 1(b)), and the others have no characteristic feature (Fig. 1(c)).

The chemical microanalysis results are reported in Table 1. Some analyses were performed on the initial silicon particles in order to take into account the contribution of the backscattered electrons which may have induced some artefacts by adding a chemical contribution of the walls of the SEM chamber after interaction of the former with the latter. The chemical analyses of the initial silicon particles were determined by neutron activation analyses [24]: $\text{Fe} \leq 10^{14} \text{ at. cm}^{-3}$, $\text{Cr} \leq 5 \times 10^{12} \text{ at. cm}^{-3}$. Therefore, the iron and chromium contributions have to be considered as the background noise of the SEM analyses and must be subtracted from the concentration which is measured on the ball-milled silicon powders. Table 1 presents the results before (1) and after (2) taking into account the (Fe, Cr) background contribution. Then the total mean contamination with iron and chromium is less than 0.2 at.%.

3.2. X-ray investigations

3.2.1. As-ball-milled powders

Figures 2(a), 3(a) and 4(a) show the various X-ray diffraction patterns which have been obtained for Si(I), Si(II) and Si(III) respectively.

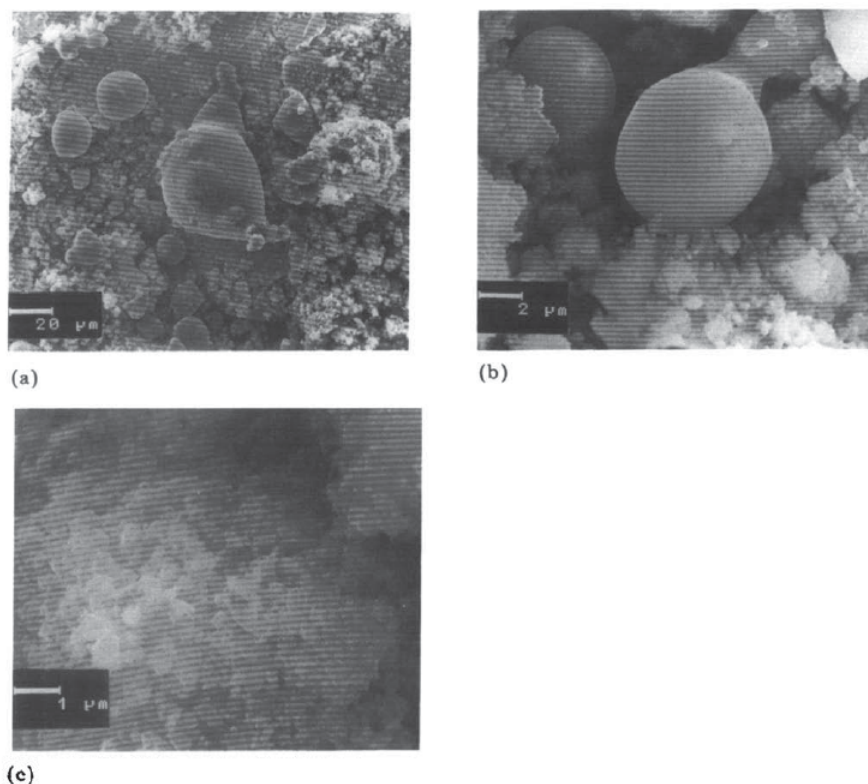


Fig. 1. (a) Typical scanning electron micrograph of the ball-milled silicon powder; (b) and (c) show detailed views of the two kinds of particles. (Secondary electron image mode.)

TABLE 1

EDX microanalysis results (at.%) of the ball-milled powder as a function of the ball-milling conditions

<i>Silicon sample</i>	<i>Ball-milling conditions</i>	<i>Silicon</i>	<i>Iron</i>	<i>Chromium</i>	
Si(I)	P7/2	99.8	0.2	0.1	(1)
		99.8	0.1	0.1	(2)
Si(II)	P5/2(10)	99.7	0.2	0.1	(1)
		99.8	0.1	0.1	(2)
Si(III)	P5/2(5)	99.8	0.2	n.d.	(1)
		99.9	0.1	n.d.	(2)
Initial Si		99.9	0.1	n.d.	

n.d. not detected or less than 0.05 at.%.

(1) Result without taking into account the backscattered electrons contribution; (2) taking into account the latter; for more details see text.

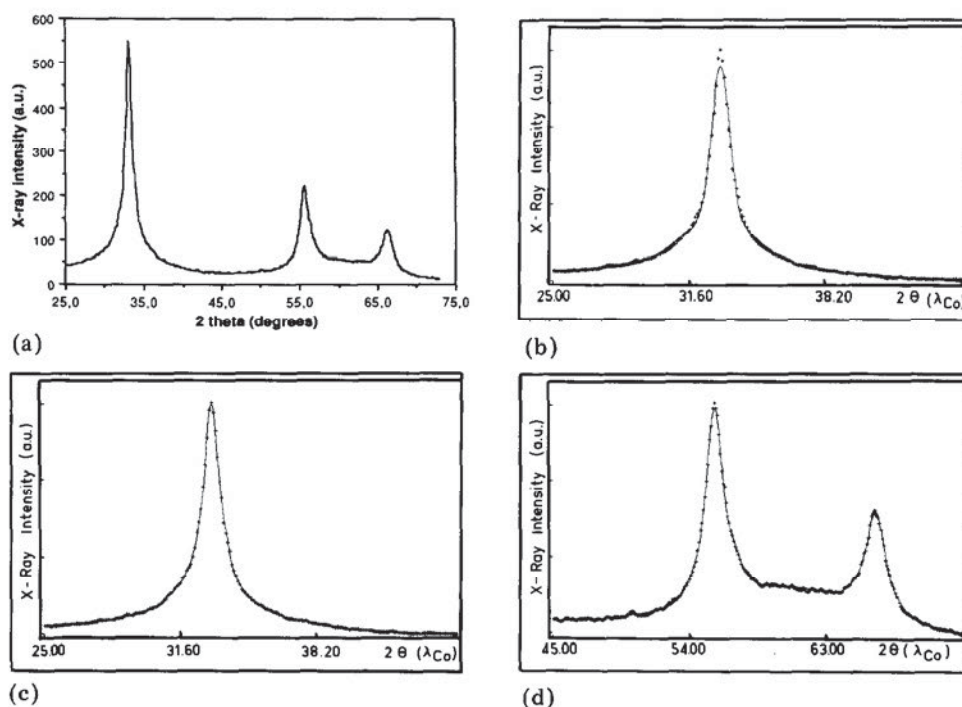


Fig. 2. (a) X-ray diffraction pattern corresponding to Si(I); (b) the curve fit obtained with one size of particles plus an amorphous phase; (c) and (d) the curve fit obtained with two sizes of particles plus an amorphous phase.

The best fit which may be obtained by the *ABFfit* program is the one which is in good agreement with the criteria which have been mentioned before. For example, Tables 2(a), 3(a) and 4, and Figs. 2(b), 3(b) and 4(b) give the results of the deconvolution of the spectra corresponding to Si(I), Si(II) and Si(III) respectively, with a model of particles such as one effective particle size plus an amorphous phase. It is clear that such a particle model does not lead to an optimized deconvolution for Si(I) and Si(II) at least. Tables 2(b) and 3(b), and Figs. 2(c, d) and 3(c, d) give the result of some deconvolution taking into account two effective particle sizes plus an amorphous phase, and corresponding to the best fit.

Applying the Scherrer formula in order to determine the effective mean size of such particles (Φ), it also appears that when the fit is correctly adjusted, the various particles may be classified as microcrystallites, nanocrystallites and amorphous phase. The expression “nanocrystallites” is based on a previously published paper from Haubold *et al.* [25]: the nanocrystalline materials are polycrystals in which the diameter of the individual crystallites is of the order of a few (typically 5 - 15) nanometers.

Such a classification appears to be schematic since, in the *ABFfit* program, it is not possible to introduce a continuous variation in the effec-

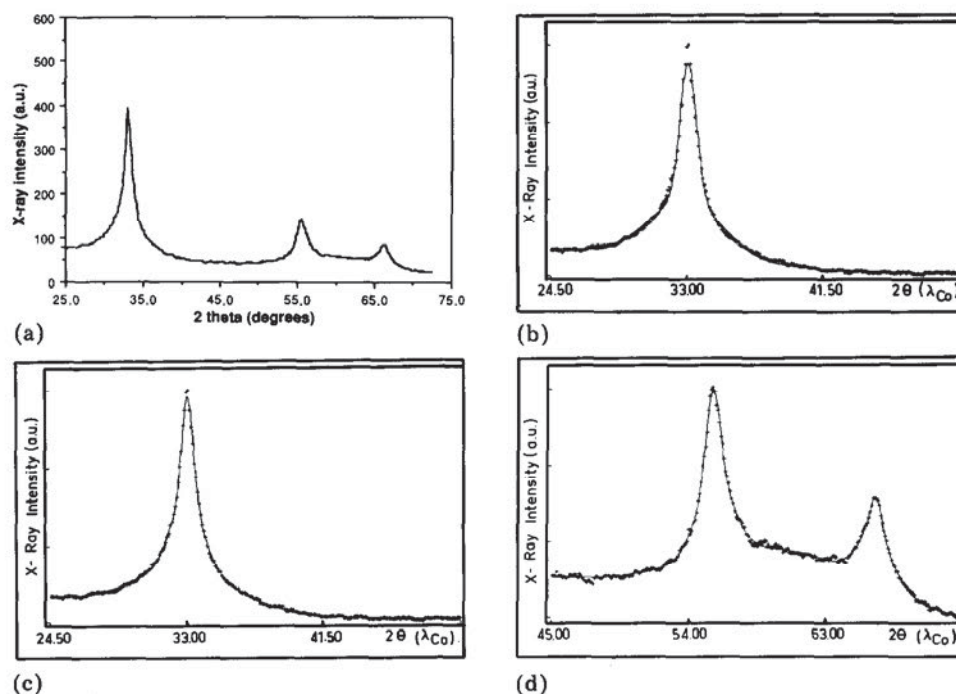


Fig. 3. (a) X-ray diffraction pattern corresponding to Si(II); (b) the curve fit obtained with one size of particles plus an amorphous phase; (c) and (d) the curve fit obtained with two sizes of particles plus an amorphous phase.

tive size of the particles. Nevertheless, qualitatively it gives the range of the effective diameters of the particles.

As shown in the Tables 2 - 4, the deconvolutions based on the different peak shapes (*i.e.* gaussian, Lorentz or Cauchy) lead to the same results. Therefore, we will choose only to discuss the X-ray results obtained from a deconvolution based on the gaussian peak shapes.

3.2.2. Recrystallized silicon powders (*in situ* DSC annealing at 725 °C)

Table 5 gives the result of the X-ray spectrum deconvolution (Fig. 5) which corresponds to the *in situ* DSC annealed silicon particles at 725 °C. It is shown that only crystalline peaks are observed; there is no diffuse peak. It should be noted that the same results are observed after X-ray spectrum deconvolution corresponding to the initial silicon particles.

So, when a silicon sample does not contain any amorphous phase (for example the initial silicon particle with a grain size of about 60 nm, or after annealing at high temperature), no diffuse peak contribution is noted. So, by comparison between the X-ray spectrum deconvolutions obtained from the crystalline silicon and the ball-milled silicon powder, the detection of the amorphous phase in the end-product of the ball-milling is clear and unambiguous. In the first case, *i.e.* crystalline silicon powder, no diffuse

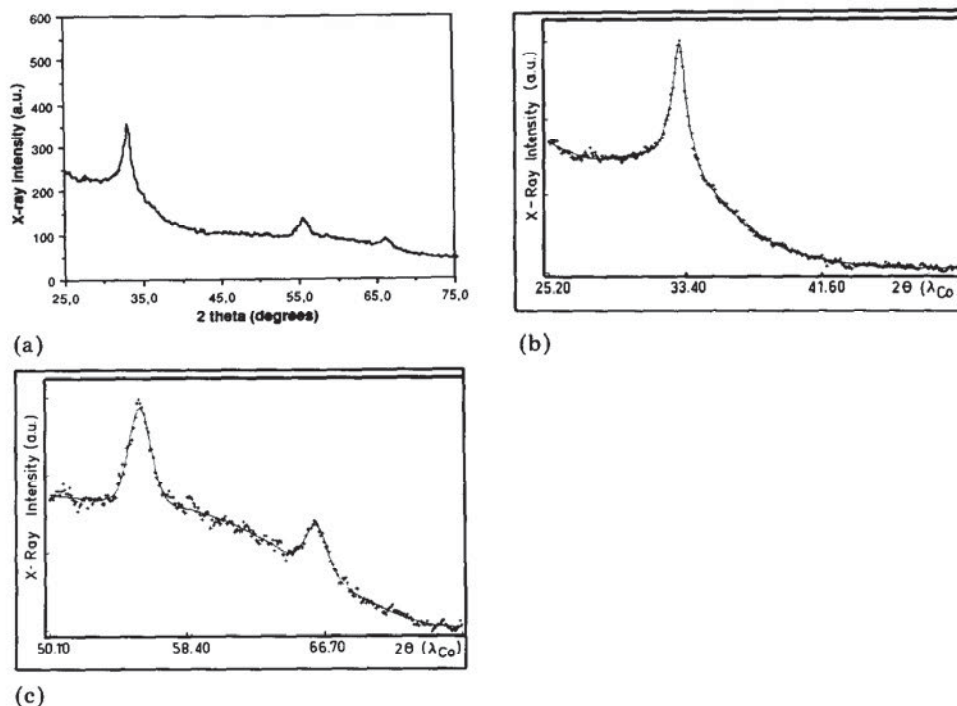


Fig. 4. (a) X-ray diffraction pattern corresponding to Si(III); (b) the curve fit obtained with one size of particles plus an amorphous phase; (c) the curve fit obtained with two sizes of particles plus an amorphous phase.

peak contribution (corresponding to the first amorphous silicon phase) in the [111] peak may be noted, and no diffuse broad peak contribution (corresponding to the second amorphous halo) may be observed between the [220] and [311] peaks.

3.3. TEM

Figure 6 shows a typical selected area diffraction pattern on which the typical microcrystalline structure is revealed. Furthermore, in spite of the fact that the rings corresponding to the [220] and [311] indexes exhibit some clear spots, the first ring exhibits a continuous diffuse intensity. This may be explained by an overlap of different contributions. Indeed, as shown by the X-ray diffraction pattern study, the first ring corresponding to the first distance [111] in silicon has several contributions: two (at least) crystalline contributions plus the first diffuse halo corresponding to the presence of the amorphous phase. Such an overlap will lead to a continuous diffuse intensity for the first ring.

Furthermore, between the [220] and [311] rings, a diffuse intensity is observed (indicated by an arrow). It corresponds to the second diffuse peak (second shoulder) of the amorphous phase. Such an electron diffraction

TABLE 2(a)

Results of the *ABFit* program (crystalline silicon particle with one effective diameter plus one amorphous phase) obtained with the various method of deconvolution models (Gauss, Lorentz, Cauchy)

	2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
Gauss	33.00	0.3149	4.29	First amorphous halo	
	33.12	0.3138	1.01	19.21	0.54355
	55.67	0.1916	1.81	11.65	0.54182
	60.18	0.1784	14.56	Second amorphous halo	
	66.25	0.1637	1.81	12.29	0.54286
Lorentz	32.98	0.3152	4.75	First amorphous halo	
	33.12	0.3138	0.96	20.4	0.54355
	55.65	0.1916	1.61	13.1	0.54200
	60.12	0.1786	13.93	Second amorphous halo	
	66.24	0.1637	1.72	12.9	0.54293
Cauchy	32.89	0.3159	5.88	First amorphous halo	
	33.12	0.3139	0.98	19.8	0.54355
	55.66	0.1916	1.54	13.7	0.54191
	60.58	0.1777	11.94	Second amorphous halo	
	66.23	0.1637	1.68	13.2	0.54301

Ball-milling conditions: P7/2 95H — Si(I).

θ , peak position; d corresponding parameter obtained from Bragg's law; $FWHH$, full width at half-height; Φ , effective diameter of the grains determined from the Scherrer relation; a , lattice parameter.

TABLE 2(b)

Results of the *ABFit* program (crystalline silicon particle with two different effective diameters plus one amorphous phase) obtained with the various method of deconvolution models (Gauss, Lorentz)

	2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
Gauss	33.01	0.3148	7.53	First amorphous halo	
	33.05	0.3145	2.36	8.2	0.54467
	33.13	0.3138	0.80	24.3	0.54339
	55.60	0.1918	0.96	22.0	0.54244
	55.75	0.1913	2.65	8.0	0.54110
	60.27	0.1782	13.64	Second amorphous halo	
	66.21	0.1638	2.56	8.7	0.54315
	66.27	0.1637	1.05	21.0	0.54272
Lorentz	32.91	0.3158	8.49	First amorphous halo	
	33.05	0.3144	2.36	8.3	0.54467
	33.12	0.3138	0.79	24.6	0.54355
	55.58	0.1918	0.89	23.7	0.54262
	55.75	0.1913	2.32	9.1	0.54110
	60.53	0.1775	13.24	Second amorphous halo	
	66.20	0.1638	2.28	9.8	0.54084
	66.28	0.1636	1.09	20.4	0.54264

Ball-milling conditions: P7/2 95 H — Si(I).

See Table 2(a) for details.

TABLE 3(a)

Results of the *ABFit* program (crystalline silicon particles with one effective diameter plus one amorphous phase) obtained with the various method of deconvolution models (Gauss, Lorentz, Cauchy)

	2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
Gauss	32.90	0.3159	5.45	First amorphous halo	
	33.07	0.3143	1.21	16.1	0.54435
	55.64	0.1917	1.84	11.5	0.54209
	59.83	0.1794	14.83	Second amorphous halo	
	66.26	0.1637	1.98	11.2	0.54279
Lorentz	32.85	0.3163	5.56	First amorphous halo	
	33.07	0.3143	1.11	17.6	0.54435
	55.64	0.1917	1.72	12.3	0.54209
	59.97	0.1790	15.0	Second amorphous halo	
	66.26	0.1637	1.91	11.3	0.54279
Cauchy	32.77	0.3171	6.15	First amorphous halo	
	33.07	0.3143	1.13	17.3	0.54435
	55.63	0.1917	1.69	12.5	0.54218
	60.32	0.1780	13.82	Second amorphous halo	
	66.25	0.1637	1.95	11.4	0.54286

Ball-milling conditions: P5/2 (10) 70H.BM.

See Table 2(a) for details.

TABLE 3(b)

Results of the *ABFit* program (crystalline silicon particles with two effective diameters plus one amorphous phase) obtained with the various method of deconvolution models (Gauss, Lorentz)

	2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
Gauss	32.84	0.3165	7.08	First amorphous halo	
	33.02	0.3148	2.28	8.6	0.54515
	33.08	0.3142	0.80	24.0	0.54419
	55.60	0.1918	1.12	18.8	0.54244
	55.72	0.1914	2.90	7.3	0.54137
	60.30	0.1781	14.28	Second amorphous halo	
	66.22	0.1637	2.55	8.7	0.54308
	66.26	0.1637	0.91	24.5	0.54276
Lorentz	32.77	0.3170	6.46	First amorphous halo	
	33.06	0.3144	0.59	32.9	0.54451
	33.07	0.3143	1.57	12.4	0.54435
	55.62	0.1917	1.34	15.8	0.54227
	55.67	0.1916	2.69	7.8	0.54182
	60.15	0.1785	18.23	Second amorphous halo	
	66.23	0.1637	1.97	11.3	0.54301
	66.28	0.1636	0.69	32.5	0.54264

Ball-milling conditions: P5/2 (10) 70H.BM — Si(II).

See Table 2(a) for details.

TABLE 4

Results of the *ABFfit* program (crystalline silicon particles with one effective diameter plus one amorphous phase) obtained with the Gauss deconvolution model

	2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
Gauss	32.98	0.3151	4.73	First amorphous halo	
	33.12	0.3138	0.95	10.2	0.54355
	55.52	0.1920	1.57	6.7	0.54316
	59.62	0.1799	21.79	Second amorphous halo	
	66.20	0.1638	1.55	7.2	0.54322

Ball-milling conditions: P5/2 (5) 96H.BM — Si(III).

See Table 2(a) for details.

TABLE 5

Results of the *ABFfit* program (crystalline silicon particle with three different effective diameters) obtained with the Gauss deconvolution models

2θ	d (nm)	$FWHH$	ϕ (nm)	a (nm)
33.06	0.31469	3.58	5.4	0.5451
33.18	0.31323	1.26	15.5	0.5425
33.22	0.31289	0.44	45	0.5419
55.68	0.19153	0.60	35	0.5417
55.76	0.19128	1.81	12	0.5410
56.23	0.18981	6.42	33	0.5369
65.09	0.16627	6.31	35	0.5515
66.31	0.16355	1.77	12.5	0.5424
66.34	0.16348	0.60	37	0.5422

After *in situ* DSC annealing at 725 °C.

See Table 2(a) for details.

pattern is in good agreement with the previous analyses of the X-ray diffraction patterns.

As the diameter of the selected area is on the micrometer scale, we may affirm that both structures, *i.e.* crystalline (microcrystalline and/or nanocrystalline) and amorphous, coexist on the micrometer scale.

3.4. DSC

The thermal traces corresponding to the low-temperature range (between 100 and 350 °C) will be discussed later.

Typical DSC traces obtained with two different heating rates are shown in Fig. 7. For high heating rates, (Fig. 7(a), 40 °C min⁻¹, Table 6) three major effects are detected: an exothermic contribution below 520 °C, an endothermic event between 520 and 630 °C, and an exothermic peak above 630 °C. The first two effects will be described below. As will be

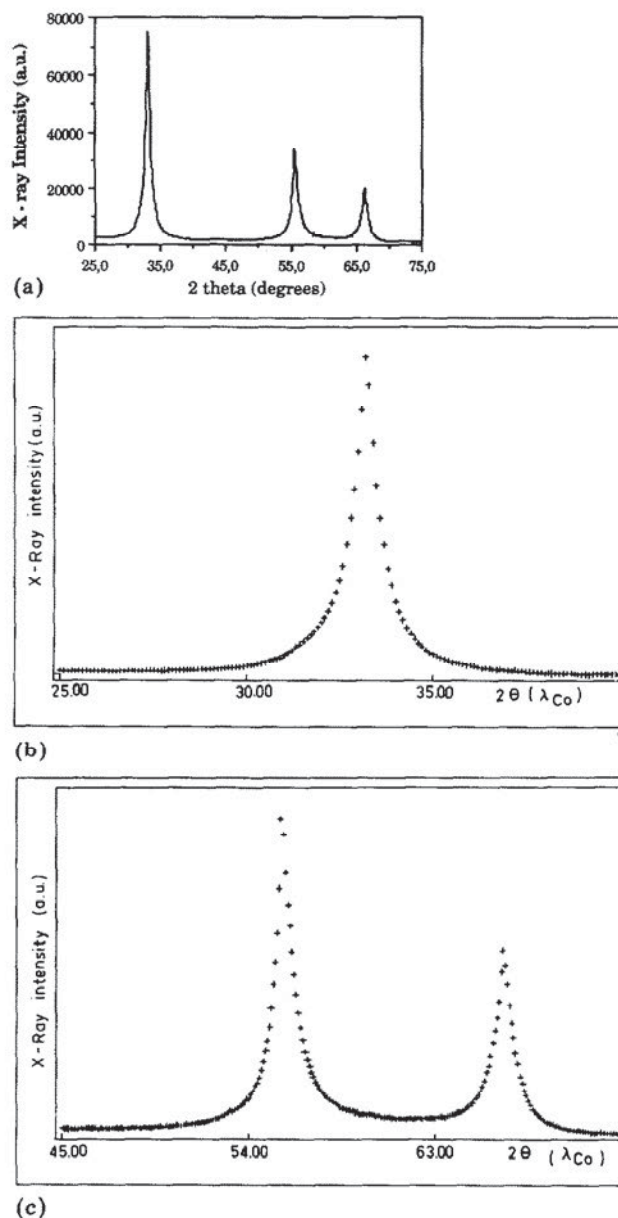


Fig. 5. (a) X-ray diffraction patterns corresponding to the *in situ* DSC annealed powders at 725 °C; (b) and (c) the curve fit obtained with three sizes of particles.

discussed in Section 3.4.1, the high-temperature peak starting from 630 °C is due to the amorphous–crystalline phase transition.

For the low heating rate (Fig. 7(b), 2.5 °C min⁻¹, Table 6), the crystallization is almost complete at 725 °C. It should be noted that the crystallization peak position is at 694 °C and 720 °C for heating rates of 2.5 °C min⁻¹

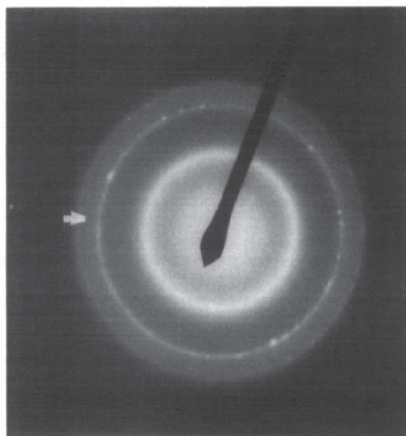


Fig. 6. Typical SAD pattern of the ball-milled silicon powder (the diameter of the selected area is about $2\ \mu\text{m}$).

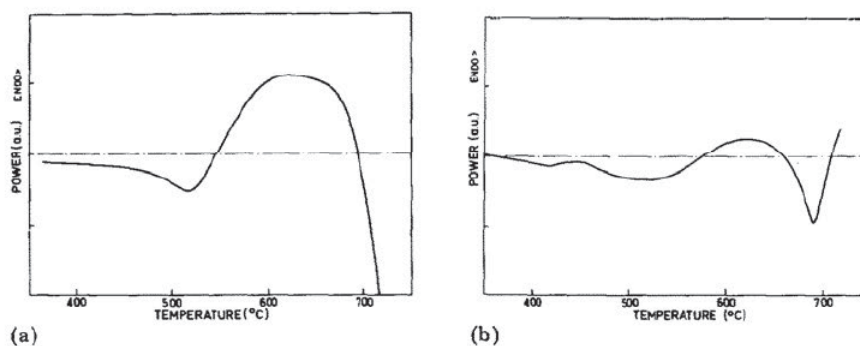


Fig. 7. (a) DSC traces of Si(III) at heating rate of $40\ ^\circ\text{C min}^{-1}$ corresponding to the run "E-I". The experimental details are listed in Table 6: (b) DSC traces of Si(III) at heating rate of $2.5\ ^\circ\text{C min}^{-1}$ corresponding to the run "B-D". The experimental details are listed in Table 6.

and $10\ ^\circ\text{C min}^{-1}$ respectively. It was not possible to record the whole crystallization peak for heating rates higher than $10\ ^\circ\text{C min}^{-1}$ since it was outside the range of the DSC apparatus.

Below the crystallization temperature, different thermal responses are observed by comparison with high-temperature rates. They are discussed below.

3.4.1. Structural state after *in situ* DSC annealing up to $725\ ^\circ\text{C}$

The main result of the X-ray investigation (X-ray pattern (Fig. 5) and *ABFfit* deconvolution program (Table 5)) is the fact that no more diffuse peaks (corresponding to the first and second halos of the amorphous silicon

TABLE 6

Experimental details of the DSC runs corresponding to Figs. 7(a), 7(b), 8(a), 8(b) and 9

Run	Heating rate ($^{\circ}\text{C min}^{-1}$)	$T_{\min}$ ($^{\circ}\text{C}$)	$T_{\max}$ ($^{\circ}\text{C}$) (<i>dwell time</i> $T_{\max}$)
Fig. 7(a)			
A	40	50	350 (6 min)
B-D	2.5	350	450 (1 min)
E-I ^a	40	350	725 (1 min)
J, K ^b	2.5	350	725 (1 min)
Fig. 7(b)			
A	40	50	350 (6 min)
B-D ^a	2.5	350	725 (2 min)
Figs. 8(a) and 9			
A-C	40	50	350 (1 min)
D-G	40	50	570 (1 min)
H-K ^a	40	50	725 (2 min)
Fig. 8(b)			
A-C	40	50	450 (1 min)
D-G	40	50	725 (1 min)
H-I ^a	40	50	725 (2 min)

^aReference baseline.^bReference baseline (Fig. 7(a), heating rate: $2.5^{\circ}\text{C min}^{-1}$).

phase) are observed. Therefore, the *in situ* DSC annealed end-product is crystalline. The whole thermal response from room temperature up to 725°C contains the exothermic crystallization process.

Furthermore, for deconvolution, three discrete particle sizes were used: 4 ± 0.5 , 13 ± 2.5 and 39 ± 6 nm. By comparison with the as-ball-milled particle sizes, an increase in diameter of the pre-existent crystalline grains is observed, the low particle sizes corresponding in such a case to the product of the crystallization of the amorphous phase.

3.4.2. Thermal stability at a low heating rate ($2.5^{\circ}\text{C min}^{-1}$, above 350°C)

The DSC traces of the Si(III), *i.e.* P5/2(5) using a heating rate of $2.5^{\circ}\text{C min}^{-1}$ is presented in Fig. 7(b). The response appears somewhat complicated and may be decomposed into three major contributions. Going from the lower to the higher temperatures on Fig. 7(b), it can be seen that there is a low-temperature exothermic event ($350 - 570^{\circ}\text{C}$), an intermediate endothermic peak ($570 - 650^{\circ}\text{C}$) and a high temperature exothermic effect. Furthermore, a small endothermic effect ($420 - 470^{\circ}\text{C}$) seems to overlap the low-temperature exothermic peak. Another possible interpretation may be to invoke two successive exothermic contributions but further discussions will show it to be inconsistent.

In order to investigate the various contributions (*i.e.* endothermic and exothermic), different runs were performed. As an endothermic event may be reversible, some cycles were undertaken in order to study the broad intermediate endothermic peak and the small endothermic one superimposed on the low-temperature exothermic event.

3.4.3. Thermal stability at high heating rate ($40\text{ }^{\circ}\text{C min}^{-1}$). Below $350\text{ }^{\circ}\text{C}$: low-temperature exothermic and endothermic contributions

The various heating conditions for the DSC experiments are listed in Table 6 and the corresponding thermal responses of the sample are presented in Fig. 8(a) and 8(b) respectively.

In the temperature range from 100 to $350\text{ }^{\circ}\text{C}$, two effects seem to be apparent: an irreversible exothermic peak "A-K" (Fig. 8(a), curve A) and a reversible endothermic event. The questions which remain to be solved are whether the endothermic effect occurs during the first heating run and whether it is superimposed on the exothermic event. In the first case, the exothermic peak contribution corresponds to the area defined between the curves C and A (corresponding to "C-K" and "A-K"). In the other case, such an exothermic response will correspond to the area defined between the curve "J-K" and "A-K". The curve "J-K" is the horizontal curve starting in the middle of the Y axis.

In both cases, the endothermic effect corresponds to the area above "J-K". It appears that there is perfect overlapping of the thermal response between the runs "B-K" and "C-K" (Fig. 8(a)), indicating a reversible event.

In order to demonstrate the reproducibility of the various effects, another set of heating runs is presented in Fig. 8(b) (the related parameters are listed in Table 6) and is consistent with the above description corresponding to Fig. 8(a).

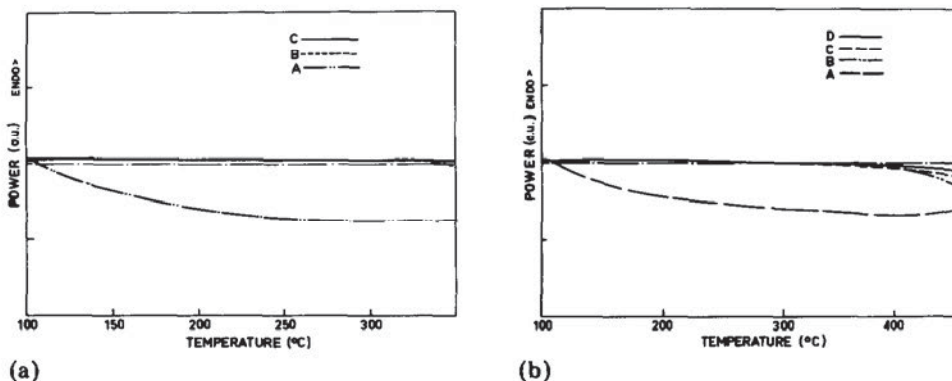


Fig. 8. Investigations of the low temperature exo- and endothermic peaks. (a) DSC traces at heating rate of 40 K min^{-1} corresponding to the runs "A-K", "B-K" and "C-K" (temperature range $100 - 350\text{ }^{\circ}\text{C}$). The experimental details are listed in Table 6. (b) DSC traces at heating rate of 40 K min^{-1} corresponding to the runs "A-I", "B-I", "C-I" and "D-I" (temperature range $100 - 450\text{ }^{\circ}\text{C}$). The experimental details are listed in Table 6.

3.4.4. Thermal stability at high heating rate ($40\text{ }^{\circ}\text{C min}^{-1}$). — Between 350 and $570\text{ }^{\circ}\text{C}$ (below the crystallization): broad intermediate temperature endothermic event

Figure 9 (Table 6) shows the thermal effects which have been observed with the specimen corresponding to Fig. 8(a) after thermal treatments below $350\text{ }^{\circ}\text{C}$.

A residual exothermic contribution is observed in curve D. It appears to be the end of the low exothermic peak which is observed on Curve A of Fig. 8(a) corresponding to the same set of runs.

Curve E (corresponding to "E-K") also shows a slight exothermic contribution which has not been completed during the previous run D.

From this run E, no more irreversible low-temperature exothermic contribution appears, and only the reversible effect is shown. As was the case for the previous weak low-temperature endothermic contribution, there is perfect overlapping of the thermal response between successive cycles (F to H) in the temperature range between 300 and $400\text{ }^{\circ}\text{C}$ (Fig. 9, heating conditions Table 6).

Nevertheless, as the temperature is relatively high at the end of each run ($725\text{ }^{\circ}\text{C}$), some crystallization event occurs leading to an exothermic contribution which becomes progressively more effective as the number of cycles increases, since the previous crystalline areas may act as sites of easy crystallization of the remaining amorphous phases.

The crystallization peak position is at $694\text{ }^{\circ}\text{C}$ and $720\text{ }^{\circ}\text{C}$ for heating rates of $2.5\text{ }^{\circ}\text{C min}^{-1}$ and $10\text{ }^{\circ}\text{C min}^{-1}$ respectively.

After crystallization, the endothermic peak at intermediate temperature ($350 - 570\text{ }^{\circ}\text{C}$) completely disappears. Thus the endothermic peak is correlated with the amorphous phase thermal response.

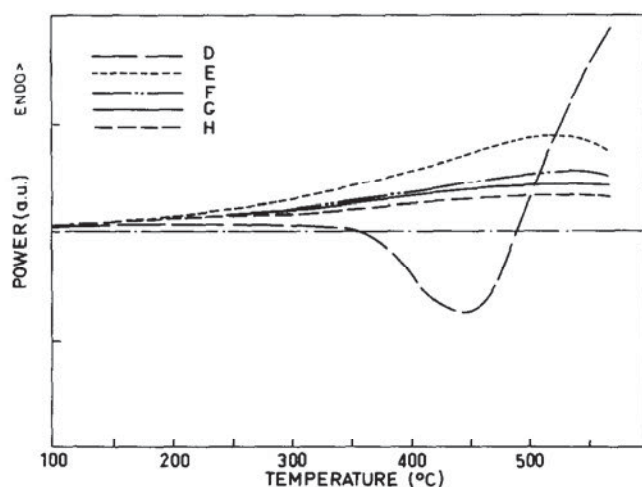


Fig. 9. Investigations of the intermediate temperature endothermic peak: DSC traces of Si(III) at heating rate of 40 K min^{-1} corresponding to the runs "D-K", "E-K", "F-K", "G-K" and "H-K". The experimental details are listed in Table 6.

4. Discussion

The above experimental results lead to the existence of a dynamic equilibrium between the amorphous silicon phase and the polycrystalline silicon phase induced by ball-milling.

The meaning of the expression “dynamic equilibrium induced by ball-milling” has previously been explained [6]: the formation of the various phases during ball-milling is not just the result of enhanced diffusion and is not driven by the usual thermodynamic potential. As mentioned in ref. 6, a similar situation is well known for alloys under irradiation, where in some cases the appropriate driving force for phase changes has been identified and implies the alloy composition and temperature plus a dynamic variable which scales with the power injected in the alloy [26, 27].

From our knowledge, this is the first time that a ball-milling process has succeeded in such a transition starting from a pure element *i.e.* silicon. Other techniques lead to a silicon amorphous phase, vapour deposition [28], laser surface treatment [29] or ion irradiation with 1.8 MeV krypton ions [30]. Nevertheless, such techniques only lead to the formation of a thin film (vapour deposition) or modify a thin layer of the exposed surface of the material (laser and/or ion irradiation). Further investigations and a better knowledge of the mechanism of phase transition may lead to a three-dimensional amorphous silicon phase by ball-milling.

In such a perspective, it is interesting to note the value of the lattice parameter a as a function of the various ball-milling conditions. As explained in Section 2, the *ABFfit* program which has been used does not allow us to determine the gradual variation of the particle size but leads to a discretization of the grain size distribution. Though such a classification is effectively rather schematic, it nevertheless allows us to compare the range of the lattice parameter as a function of the grain size and of the ball-milling conditions. Such a classification may be obtained from Tables 2(b), 3(b) and 4. This leads to the following mean values:

Si(I)	$\Phi \approx 8 \text{ nm}$	$a_1 = (0.5435 \pm 0.0015) \text{ nm}$
	$\Phi \approx 20 \text{ nm}$:	$a_2 = (0.5425 \pm 0.0015) \text{ nm}$
		$(a_1 - a_2)/a_2 \approx 0.2\%$
Si(II)	$\Phi \approx 8 \text{ nm}$:	$a_1 = (0.5435 \pm 0.0020) \text{ nm}$
	$\Phi \approx 20 \text{ nm}$:	$a_2 = (0.5430 \pm 0.0020) \text{ nm}$
		$(a_1 - a_2)/a_2 \approx 0.1\%$
Si(III)	$\Phi \approx 8 \text{ nm}$:	$a = (0.5430 \pm 0.0025) \text{ nm}$
		$(a_1 - a_0)/a_0 \approx 0\% (a_0: \text{see below})$

It should be noted that the value of the lattice parameter corresponding to the larger particle size (a_2) is in agreement with that obtained by Kiendl [31]: $a_0 = 0.54310 \text{ nm}$, the lattice parameter corresponding to the lower par-

ticle size exhibits a relative difference of 0.2% for Si(I) and 0.1% for Si(II).

Such an observation is in agreement with the results obtained by Veprek *et al.* [28]. Indeed, the authors studied the formation of amorphous silicon during condensation from the vapour phase. They noticed the change in the crystal lattice parameter as a function of the crystal particle size: for a crystal particle size larger than about 9 - 10 nm, the lattice parameter is equal to a_0 . Below 9 - 10 nm, the lattice parameter grows with reduction in particle size. When the crystal particle size reaches 3 nm, the lattice parameter has risen by about 1%. Below the critical particle size (hereafter referred as Φ_c , and the related lattice parameter change Δa_c), the diamond lattice becomes unstable and crystalline silicon transforms into the amorphous phase. Such is the case for unconstrained silicon films, under conditions of compression, the crystal-amorphous phase occurs with a smaller particle size of about $\Phi_c = 2$ nm and the lattice parameter variation is lower: $\Delta a_c = 0.6\%$.

According to the results of the various deconvolutions leading to the determination of the different sizes of the silicon crystalline particles which are in dynamic equilibrium with the amorphous phase, the critical particle size and the corresponding lattice expansion at which the diamond lattice becomes unstable with respect to the amorphous phase under the ball-milling conditions which have been used in our experiments, can be estimated to be:

Si(I)	$\Phi_c = 8$ nm	$\Delta a_c \approx 0.2\%$
Si(II)	$\Phi_c = 8$ nm	$\Delta a_c \approx 0.1\%$
Si(III)	$\Phi_c = 8$ nm	$\Delta a_c \approx 0.0\%$

Therefore, the crystal-amorphous phase transition may be explained by a refinement of the grain size of the particle which leads to a destabilization of the diamond structure; the critical size of the particle does not seem to be affected by the ball-milling conditions but the Δa_c value shows a strong correlation with the latter: the higher the energy input during the ball-milling, the larger the value of Δa_c .

It appears that continuous ball-milling, *i.e.* fracturing and cold welding, leads to an effective grain size ranging from 20 to 8 nm for the crystals: the higher energetic conditions (P7/2) seem to be able to stabilize the highly deformed lattice, so it is possible to observe crystals with a mean diameter of 8 nm with a higher value of Δa_c , as in the case of Si(I) and Si(II), and not in the case of Si(III). In this latter case, the refinement of the grain size to a scale of about 8 nm, in Si(III) conditions, leads to a direct destabilization even in the case of low Δa_c . Such considerations may be deduced from the deconvolutions of the X-ray patterns. It is obvious that further TEM investigations at a microstructural scale must be performed in order to confirm these macroscopic observations.

Let us now consider the thermal behaviour during the DSC experiments. It should be noted that the same kinds of contributions, *i.e.* a low-temperature exothermic peak, an intermediate-temperature endothermic

peak and a high-temperature exothermic crystallization event have been also encountered for the Ni-Zr system [15]. In ref. 15, the origin of the various peaks have been interpreted as a relaxation of the stressed inter-metallic compounds (exothermic contribution), followed by a local equilibration between the amorphous phases and the *in situ* relaxed compounds leading to a change in composition of the amorphous phases (endothermic effect since the heat of mixing is negative), and at higher temperature, the crystallization of the various amorphous phases (exothermic events).

Such an interpretation for the two exothermic contributions which are obtained for the ball-milled silicon thermal analysis is also consistent.

The high stability of the ball-milled silicon amorphous phase should be noted. According to Veprek *et al.* [28], a thermodynamic evaluation of the minimum size of the crystallization nuclei amounts to 3 nm (*i.e.* more than 1000 atoms); therefore a large activation energy is necessary to transform an amorphous cluster into a crystalline one of such a size. This explains the high stability of the amorphous silicon showing a recrystallization at $T_c \geq 1/2T_m$. Such a determination of the critical size for nucleation corresponds to a homogeneous nucleation.

Considering the X-ray investigations as well as the TEM observations there are some crystals which remain throughout the process and should act as "heterogenous" nuclei for crystallization. Therefore, heterogeneous nucleation should occur during the DSC heating run and such a nucleation is expected to occur at a lower temperature and with a lower activation energy with respect to a homogeneous crystallization. In fact this is not the case: the crystallization peak position of the ball-milled silicon occurs at a higher temperature than the one obtained for a silicon amorphous phase produced by Xenon implantation, *i.e.* 692 °C for a heating rate of 40 K min⁻¹ [32], or by vapour deposition. The values reported by Köster [33], are in the temperature range 450 - 700 °C, and the activation energy determined by Kissinger's method [34] is equal to 323.0 kJ mol⁻¹ (or 3.35 eV at.⁻¹) and must be compared with the one mentioned by Köster (290 kJ mol⁻¹ or 3.0 eV at.⁻¹ [33]) or reported by Zellama *et al.* [35] (231.6 kJ mol⁻¹ or 2.4 eV at.⁻¹). Such a result has been observed for the Ni-Zr system which exhibits a higher activation energy for the crystallization of the ball-milled Ni₅₅Zr₄₅ amorphous phase (3.8 eV at.⁻¹) than for the melt-spun ribbons of the same composition (3.0 eV at.⁻¹) [15].

The various activation energy values (the previously published ones and the one obtained in the present work) which correspond to the crystallization of the amorphous phase silicon are widely dispersed. Such a dispersion is not so surprising. Indeed, Buschow [36] has determined the activation energies for the crystallization of Ni-Zr and Cu-Zr amorphous alloys which range from 2.88 to 6.81 eV at.⁻¹ (Ni-Zr system) and from 2.45 to 6.40 eV at.⁻¹ (Cu-Zr alloys). The explanation proposed was the relatively strong temperature dependence of the configurational entropy expected for alloy compositions with strong chemical short-range order which leads to an increase in the experimental values of the apparent activation energies.

A previous work [37] has studied the influence of the pre-existing crystalline nuclei upon the activation energies (nucleation and growth) of the amorphous–crystalline phase transition during annealing. In the case of the existence of pre-nuclei (before annealing), the activation energy for nucleation is higher. No major change in the activation energy corresponding to the growth kinetics is observed. Taking into account these results and our observations, we propose that during annealing, the growth of the pre-existing silicon crystallites, which remain after ball-milling, leads to a decrease in the rate of homogeneous nucleation. Indeed, as the amorphous–crystalline interface evolves, the number of nuclei which are smaller than the critical size decreases, as they are absorbed when the interface encounters them, leading to a decrease of the number of nuclei capable of reaching the critical size. Therefore, such competition between the two crystallization processes seems to result in a higher value of the activation energy for crystallization, determined by Kissinger’s formula (which includes nucleation and growth kinetics), and leads to a higher thermal stability of the ball-milled silicon powder.

5. Conclusion

To our knowledge, this is the first time that a crystal–amorphous phase transition induced by ball-milling has been observed in a pure element: in this case silicon. Based on experimental investigations (SEM, EDX, X-ray patterns, TEM, DSC experiments), it seems that the transition occurs during a continuous refinement of the grain size of the particle and a change in the lattice parameter of silicon crystals which leads to a destabilization of the diamond structure. The effects of the ball-milling conditions on such a destabilization are noted. The crystallization temperature and the activation energy for the crystallization of the ball-milled amorphous phase are much higher than those which may be obtained by melt spinning or irradiation.

Further investigations need to be performed in order to study the nature of the various interfaces between the silicon crystals and the silicon amorphous phase, for a better understanding of the elemental mechanism leading to such a transition and for determining whether one single homogeneous amorphous pure silicon phase may be obtained by such a process rather than a dynamic equilibrium between microcrystalline and amorphous states.

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