

The structure and property characteristics of amorphous/nanocrystalline silicon produced by ball milling

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The structural transformation of polycrystalline Si induced by high energy ball milling has been studied. The structure and property characteristics of the milled powder have been investigated by x-ray diffraction, scanning electron microscopy, high-resolution electron microscopy, differential scanning calorimetry, Raman scattering, and infrared absorption spectroscopy. Two phase amorphous and nanocrystalline Si has been produced by ball milling of polycrystalline elemental Si. The nanocrystalline components contain some defects such as dislocations, twins, and stacking faults which are typical of defects existing in conventional coarse-grained polycrystalline materials. The volume fraction of amorphous Si is about 15% while the average size of nanocrystalline grains is about 8 nm. Amorphous elemental Si without combined oxygen can be obtained by ball milling. The distribution of amorphous Si and the size of nanocrystalline Si crystallites is not homogeneous in the milled powder. The amorphous Si formed is concentrated near the surface of milled particles while the grain size of nanocrystalline Si ranges from 3 to 20 nm. Structurally, the amorphous silicon component prepared by ball milling is similar to that obtained by ion implantation or chemical vapor deposition. The amorphous Si formed exhibits a crystallization temperature of about 660 °C at a heating rate of 40 K/min and crystallization activation energy of about 268 kJ/mol. Two possible amorphization mechanisms, i.e., pressure-induced amorphization and crystallite-refinement-induced amorphization, are proposed for the amorphization of Si induced by ball milling.

I. INTRODUCTION

Over the last several years, a considerable amount of work has been performed on the formation of amorphous and nanocrystalline materials by mechanical attrition since it offers the possibility for production of tonnage quantities of various kinds of amorphous and nanocrystalline materials for potential applications.¹⁻³ The amorphization induced by mechanical alloying (MA) of mixtures of pure elemental crystalline powders is attributed to a solid-state interdiffusion reaction, the kinetics of which is controlled by the excess point and lattice defects. The amorphization induced by mechanical milling (MM) of crystalline intermetallic compounds is attributed to the accumulation of point and lattice defects that raise the free energy of the

defected intermetallic compound above that of the amorphous phase. As for the nanocrystalline materials, it is believed that their special properties result from the ultrafine grain size⁴ which makes the fraction of atoms that reside in grain boundaries comparable with that in the grain interior.⁵ The grain size in a series of nanocrystalline fcc metals produced by mechanical attrition saturates to a minimum value which scales with the melting point of the given elements.⁶ This implies a balance between the creation of defects and recovery or recrystallization.

The properties of nanocrystalline silicon (nc-Si) are significantly different from those of conventional polycrystalline or amorphous silicon. Therefore, interest has focused increasingly during the past several years on nc-

Si prepared by various methods because it has potential technological importance.⁷ Recently, it has been discovered that ball milling can be used to obtain crystal-to-amorphous and/or crystal-to-nanocrystalline transitions for some semiconductor elements, e.g., C,⁸ Si,^{9,10} and Ge.¹¹ However, the formation of amorphous elemental Si along with the development of a nanocrystalline structure during ball milling remains a controversial issue. Gaffet and Harmelin first reported a partial amorphization (about 10%) of Si by ball milling⁹ and found that this amorphous Si phase had a higher crystallization temperature and a higher crystallization activation energy when compared with the amorphous Si prepared by ion implantation or vapor deposition. Bokhonov *et al.*¹⁰ argued that the observed partial amorphization of pure polycrystalline silicon might be attributed to the combination of silicon and oxygen during milling such that the amorphous phase is SiO.

Results of HREM images of nanocrystalline Pd have indicated that the interface atomic structure in nanocrystalline metals is not fundamentally different from that observed in coarser-grained polycrystals.¹² More recently, fivefold twins, edge, and 60° dislocations, which are similar to those normally observed in coarse-grained polycrystals, are observed in nanocrystalline Pd.¹³ Therefore, it should be interesting to investigate the atomic structure of nanocrystalline semiconductor elements such as Si. The observation may also be helpful to the understanding of formation of amorphous and nanocrystalline structures in Si prepared by ball milling.

In the present paper, we report experimental results of ball-milled Si, which (i) verify the occurrence of partial amorphization first reported by Gaffet *et al.*, (ii) show the microstructure and thermal properties of amorphous and nanocrystalline phases formed, and (iii) indicate the possible mechanism for the amorphization of Si induced by ball milling.

II. EXPERIMENTAL

Polycrystalline Si powders of nominal purity of 99.9% and average particle size of 150 μm were used as starting materials. 2.5 g of powder were put into a hardened tool-steel vial together with 20 g of 440C martensitic stainless steel balls of diameter 6 and 8 mm. Milling was performed under argon. The vial was put into an argon-filled glovebox with oxygen content less than 3 ppm and sealed with an elastomer "O"-ring seal. The ball milling was performed in a high energy Spex-8000 shaker mill. A fan was used during the milling to keep the vial at 30 °C. X-ray diffraction (XRD) was performed with a Rigaku Geigerflex diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) and a graphite monochromator. Impurity contamination by oxygen and iron was measured using LECO TC-436 Oxygen/Nitrogen

Analyzer and argon plasma emission spectroscopy, respectively. The particle morphology was analyzed by S-530 scanning electron microscopy at an acceleration voltage of 20 kV. At least 50 separate particles were chosen for the measurement of particle size of milled powder. Thermal analysis was carried out in a differential scanning calorimeter (DSC), Du Pont model 9900, under flowing argon. The microstructure observation was performed in a top-entry JEOL 2000 EXII high-resolution electron microscope (HREM) with a point-to-point resolution of 0.21 nm. The powder preparation for HREM and transmission electron microscopy (TEM) observation consisted of mixing Si powder with ethanol and putting a drop onto a carbon-coated copper grid. The Raman spectra (RS) were excited with 150 mW of 514.5 nm radiation from an Ar ion laser, and the scattered light was dispersed with a U1000 ISA double spectrometer. The sample geometry for the RS measurements was a disk with a diameter of 3 mm and a thickness of 0.5 mm prepared by pressing the powder under a nominal pressure of 3.1 GPa. Infrared spectroscopic study was performed in an IG-10 Infrared Spectroscope. About 1 mg of powder was used for each measurement.

III. RESULTS

The sample identification (ID), milling time, particle size, and oxygen and iron content for Si after 0, 3, and 38 h of milling are shown in Table I. The iron content for Si after 3 and 38 h of milling is slight. This indicates that the possible influence of iron contamination during the milling on the phase transformation induced by the milling should be negligible.

XRD patterns in Fig. 1 show significant broadening of Bragg diffraction peaks for Si powder after 3 h and 38 h milling. The average crystallite size, as calculated from the (111), (220), and (311) Bragg reflection linewidths using the Scherrer formula,¹⁴ is approximately 13 nm and 9 nm for samples Si-3 h and Si-38 h, respectively. The evidence for the existence of amorphous Si indicated by XRD patterns is not resolvable because of the relatively small amount of amorphous phase estimated by the RS and DSC to be discussed below.

Figure 2(a) shows a bright-field HREM image of Si particles after 38 h of milling from which some nanocrystalline Si grains can be seen. The corresponding

TABLE I. The sample ID, milling time, particle size, and oxygen and iron content for Si after 0, 3, and 38 h of milling.

Sample ID	Milling time (h)	Particle size (μm)	O ₂ (at. %)	Fe (at. %)
Si-0 h	0	150	0.12	0
Si-3 h	3	0.5	2.9	0.22
Si-38 h	38	0.8	2.8	0.26

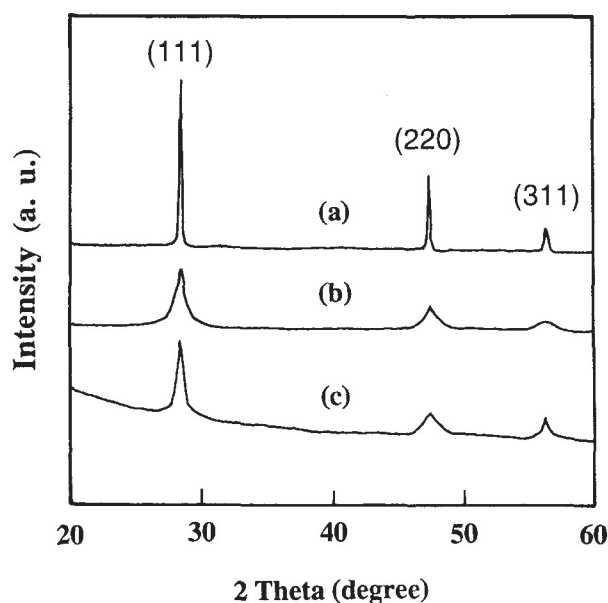


FIG. 1. XRD patterns of polycrystalline Si powders after (a) 0 h, (b) 3 h, and (c) 38 h of milling.

selected-area electron diffraction pattern for the particles also shown in Fig. 2(a) gives nearly continuous rings due to the random orientation of neighboring crystals. Furthermore, the (111) diffraction ring, which is relatively broad and exhibits inhomogeneous diffraction intensity in different orientations, indicates the possible existence of amorphous Si along with preferred orientation.

A HREM image recorded near the surface of a particle is shown in Fig. 2(b), from which one can see that the milled Si is composed of amorphous and nanocrystalline components. In this image, the two components exhibit comparable volume fraction. The size of nanocrystalline Si grains ranges from about 3 to 20 nm. The existence of abundant Si nanocrystals is shown in Fig. 2(c), which is imaged in the central part of the milled particle. Si(111) lattice fringes are clearly seen. The volume fraction of amorphous phase in this region, however, is far less than that of the crystalline phase when compared with the region shown in Fig. 2(b). This indicates that the formation of amorphous Si in the milled powder is not homogeneous.

Figure 2(d) shows that multiple twins exist in the milled Si particle. Around the twins there are some disordered regions. An intrinsic Frank dislocation existing in the multiple twin is indicated by a circle. Across this dislocation the twin plane displaces by one stacking unit to a new position, as shown by the structural model in Fig. 2(e).

Another overview of the microstructure near the surface of a milled Si particle is shown in Fig. 2(f). The imaged region consists of at least three kinds of structure: amorphous phase, distorted and disordered

grain boundary regions between or among different nanocrystallites, and ordered nanocrystalline interior. Defects, such as dislocations, stacking faults, and twins, also exist in the nanocrystalline crystallites.

Shown in Fig. 3 are the DSC scans for Si-3 h and Si-38 h. Both of the scans exhibit a broad exothermic signal over the whole temperature range and a relatively sharp exothermic signal with the maximum located at 655 °C for Si-3 h and 658 °C for Si-38 h, which are very comparable to, but lower than, the crystallization temperature, 692 °C, for ion-implanted amorphous Si at a heating rate of 40 K/min,¹⁵ and 686 °C, for amorphous Si prepared by chemical vapor deposition at a heating rate of 2.5 K/min.¹⁶ The heat release related to the broad and sharp peaks is determined to be 2.1 and 1.7 kJ/mol for Si-3 h, and 2.8 and 1.8 kJ/mol for Si-38 h, respectively. For amorphous Si prepared by ion implantation, it has been shown that there is no evidence of heat release due to relaxation,¹⁷ or that there is a low-temperature structure relaxation signal with heat release equal to one-third of that of crystallization of amorphous Si.¹⁸ Therefore, the main parts of the observed broad exothermic signal may be related to the recovery of defects in the plastically deformed nanocrystalline Si and to the growth of the nanocrystals. A broad exothermic signal and the corresponding relatively large heat release is a typical feature of most nanocrystals prepared by mechanical attrition.^{6,19} The crystallization enthalpy for completely amorphous Si prepared by ion implantation has been determined to be 11.9 kJ/mol.²⁰ Accordingly, the volume fraction of amorphous phase, i.e., the ratio of heat release related to the crystallization of the amorphous phase in the milled Si powder to the crystallization enthalpy of completely amorphous Si, is estimated to be 14% and 15% for Si-3 h and Si-38 h, respectively. The crystallization activation energy can be determined by Kissinger's method²¹

$$\ln(\phi/T_p^2) = -E/(RT_p) + C, \quad (1)$$

where ϕ is the heating rate chosen for the DSC scan, T_p the temperature corresponding to the maximum of the crystallization peak, R the gas constant, and C a constant. Accordingly, the crystallization activation energy E for the amorphous Si in the powder milled for 3 h is 268 kJ/mol, which is less than the 323 kJ/mol reported by Gaffet and Harmelin,⁹ but comparable to the 290 kJ/mol by Köster²² and the 232 kJ/mol by Zellama *et al.*²³

Figure 4 shows the Raman spectra of the Si samples. The unmilled Si [Fig. 4(a)] exhibits a relatively sharp peak with a maximum at 519 cm⁻¹ and a full width at half maximum (FWHM) of 7.3 cm⁻¹, associated with the well-known Raman-active mode of crystalline Si.

The milled Si exhibits shifted and broadened crystalline Raman peaks with maximum and FWHM of 518 cm^{-1} and 10.8 cm^{-1} for Si-3 h [Fig. 4(b)], and 517 cm^{-1} and 11.1 cm^{-1} for Si-38 h [Fig. 4(c)], respectively, which is indicative of decreased grain size.²⁴ The milled Si also exhibits an additional broad lower-frequency peak with a maximum at 479 cm^{-1} and FWHM of about 77 cm^{-1} for Si-3 h [Fig. 4(b)], and with a maximum at 478 cm^{-1} and FWHM of about 75 cm^{-1} for Si-38 h [Fig. 4(c)]. These positions of the peak maximum and FWHM related

to the additional broad low-frequency peaks are typical features of amorphous Si.^{25,26} Additionally, annealing the milled Si at 390°C resulted in very little change in the Raman spectra both in position and linewidth, as shown in Figs. 4(d) and 4(f). Annealing at 725°C , however, resulted in a drastic reduction in the amorphous component, and a narrowing and shifting to higher frequency of the crystalline component, as shown in Figs. 4(e) and 4(g). Thus, the relatively sharp exothermic peak shown in Fig. 3 can be related to crystallization, and

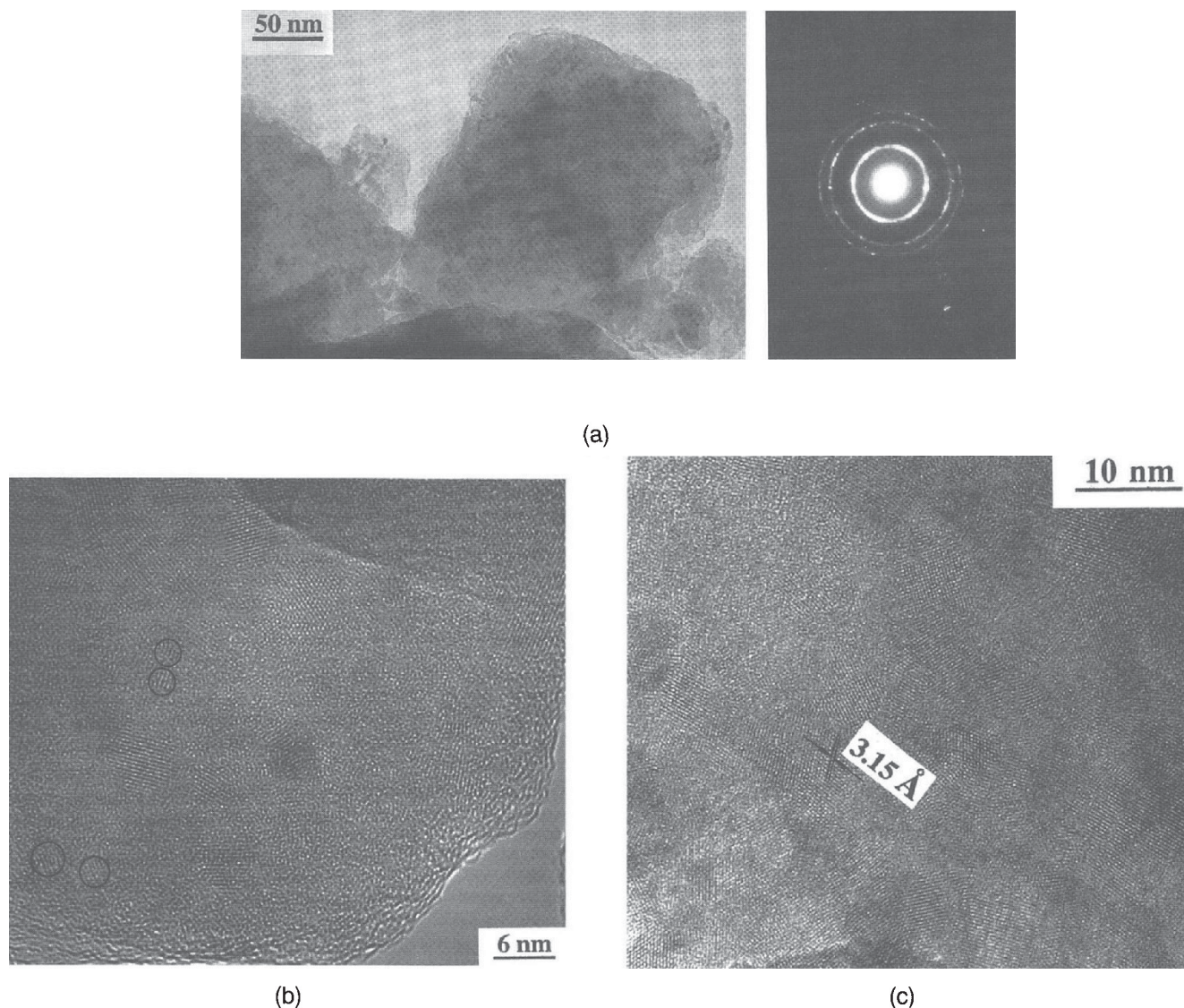


FIG. 2. TEM and HREM images of polycrystalline Si powder after 38 h of milling. (a) TEM bright-field image of Si particles and the corresponding selected-area electron diffraction pattern for the particles. (b) HREM image recorded near the surface of the particle that shows the coexistence of amorphous and nanocrystalline structures. The black circles show some nanocrystals with size of about 3 nm. (c) HREM image in the central part of the particle which indicates an abundance of nanocrystalline grains. (d) HREM image of a multiple twin around which there are some disordered regions. The circle shows an intrinsic Frank dislocation. The arrow and solid line show the twin plane on each side of the dislocation. The arrow and dashed line show other twin planes. (e) The corresponding structural model for atomic arrangement near the Frank dislocation regions shown in (d). (f) HREM image obtained near the surface of the particle shows the disordered amorphous regions, distorted and disordered nanocrystalline grain boundaries, and ordered nanocrystalline grain interior. Dislocations, stacking faults, and twins are indicated in this figure.

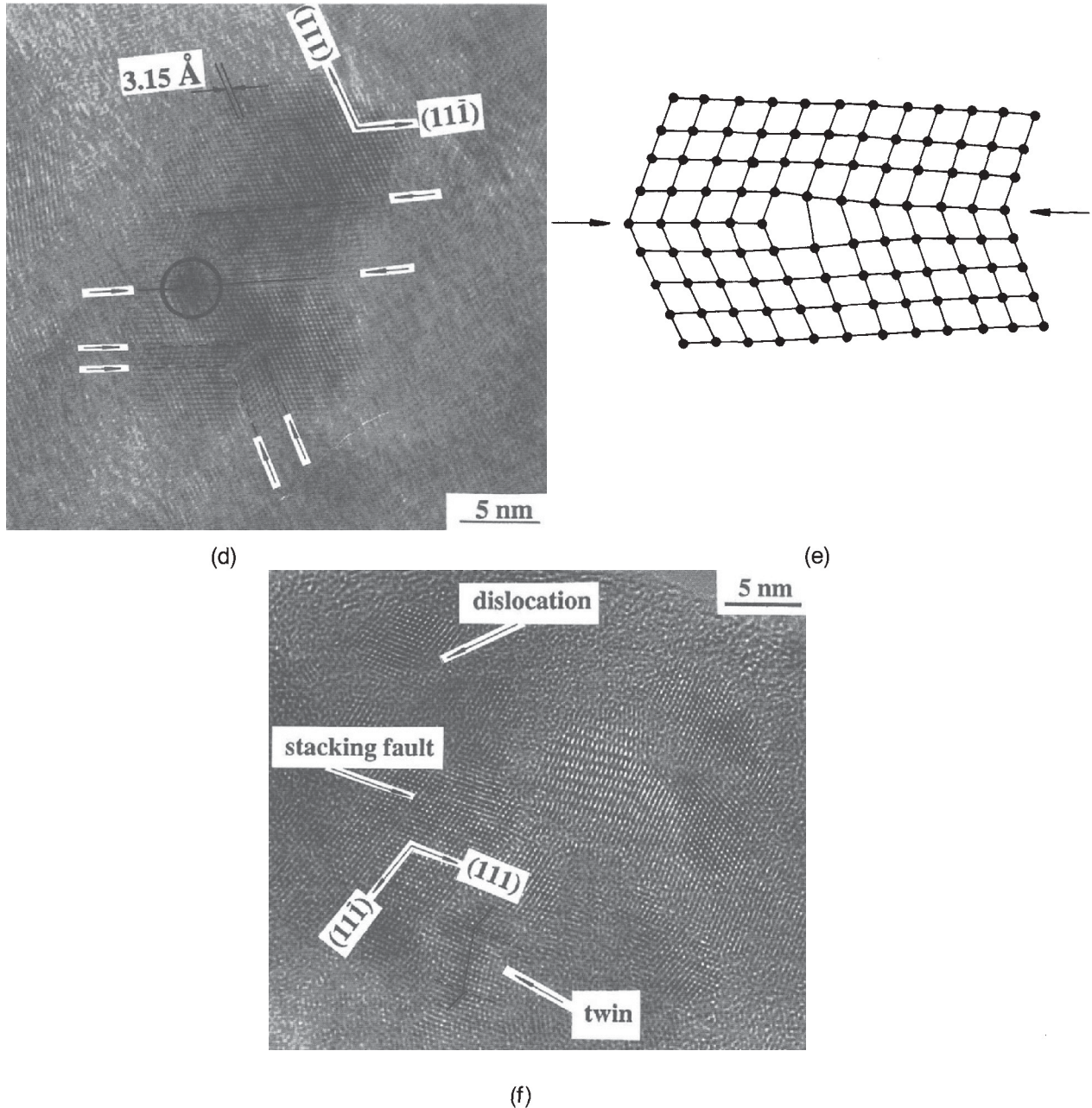


FIG. 2. (continued)

the additional wide exothermic peak over the same temperature range to the grain growth of nanocrystalline Si.

Additional information that can be extracted from the Raman spectra includes an estimate of the domain size, i.e., crystallite size, and the fractional amount of amorphous Si. Figure 5 plots the FWHM and frequency shifts extracted from the crystalline peaks of the above-mentioned Raman spectra. The data tend to follow a predicted relation for microcrystalline Si as obtained by Fauchet and Campbell.²⁷ This analysis assumed Gaussian weighting and spherical domains. Thus, the size of

the nanocrystallites formed after ball milling can be found from this relation. The crystallite size estimated is 8 nm for Si after 3 h of milling and 7 nm for Si after 38 h of milling. The fractional amount of amorphous Si can also be determined using the intensities of the amorphous and crystalline components. Nemanich *et al.*³⁸ introduce a relation used to determine this ratio:

$$I_a/I_\mu = A_a N_a V_a / (A_\mu N_\mu V_\mu) \quad (2)$$

where the subscripts *a* and *μ* refer to the amorphous and

crystalline components. I , A , N , and V are the Raman intensities, Raman cross section, atomic density, and illuminated volumes, respectively. The atomic densities can be taken as equivalent for amorphous and crystalline Si. The ratio of the Raman cross section can be determined using the peak intensities of crystalline and amorphous Si. Employing this analysis, the volume fraction of amorphous Si is found to be 0%, 33%, and 38% for Si milled for 0, 3, and 38 h, respectively.

Infrared spectra from 400 to 1600 cm^{-1} for the milled Si are shown in Fig. 6. The Si-O band, if it existed, should exhibit a peak ranging from 980 to 1082 cm^{-1} , depending on the x value in SiO_x .²⁹ It can be seen from Fig. 6 that there is a weak peak related to the Si-O band for all of the investigated samples. The peak position for Si after 3 and 38 h of milling is at about 1070 cm^{-1} and 1050 cm^{-1} , corresponding to SiO_x phases with a composition x of about 1.8 and 1.6, respectively. The peak position for Si after 3 h of milling does not exhibit an obvious shift compared with that for as-received Si, indicating that the composition of SiO_x phases does not have an apparent change. The oxygen content in the Si powder after 0, 3, and 38 h of milling is determined to be 0.12 at. %, 2.9 at. %, and 2.8 at. %, respectively. Even if all of the oxygen were combined with Si and resulted in the formation of amorphous SiO , as suggested by Bokhonov *et al.*,¹⁰ the volume fraction of the amorphous phase in the milled Si should not be larger than 6%, which is only about 40% of the volume fraction of amorphous Si estimated from the DSC signals. In fact, most of the oxygen may result from the absorption and/or adsorption of oxygen during the exposure of powder to air after the milling. The Si powder after 3 and 38 h of milling exhibits a large increase in surface area, as shown by the great change in particle size before and after milling in Table I. Moreover, the composition x for SiO_x phases estimated from the infrared spectra is greater than 1. Therefore, the interaction of oxygen and Si during milling may be negligible, and the above-mentioned 6% volume fraction of amorphous SiO is greatly overestimated. Thus, it is likely that most of the amorphous Si existing in the milled powder has not combined with oxygen.

IV. DISCUSSION

A. On the mechanism of crystal-to-amorphous transition in the milled Si powder

In comparison with the amorphization mechanisms suggested for the MA and MM processes as illustrated in Sec. I, the crystal-to-amorphous transition for pure elements, such as Si, induced by ball milling has not been well understood. Based on the results reported by other authors and obtained in the present experiments, we suggest that the amorphization mechanism for milled

Si may be one or a combination of the following mechanisms.

1. Pressure-induced amorphization

Polymorphic transformations caused by the comminution (or milling) process have been found for materials such as SiO_2 (quartz phase), metallic Co, and many

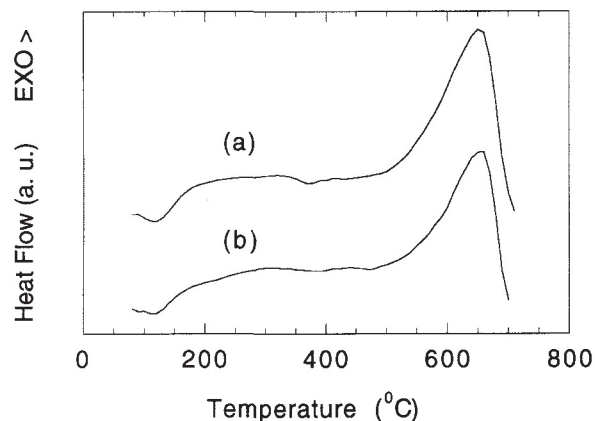


FIG. 3. DSC scans for polycrystalline Si powder after 3 h (a) and 38 h (b) of milling. Scanning rate: 40 K/min.

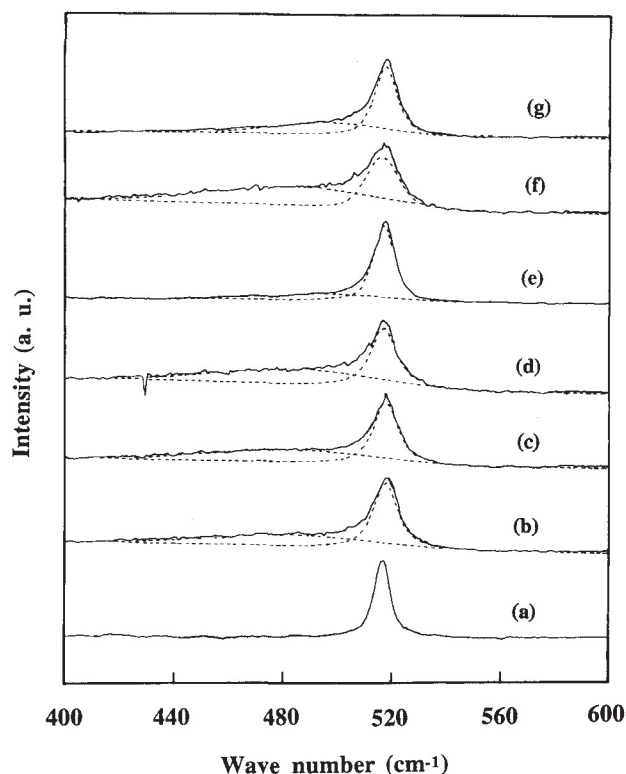


FIG. 4. Raman spectra for polycrystalline powder after 0 h (a), 3 h (b), and 38 h (c) of milling, for Si-3 h after annealing at 390 °C (d) and 725 °C (e) for 15 min, and for Si-38 h after annealing at 390 °C (f) and 725 °C (g) for 15 min, respectively. The solid lines are experimentally obtained spectra. The dashed lines are fitted spectra.

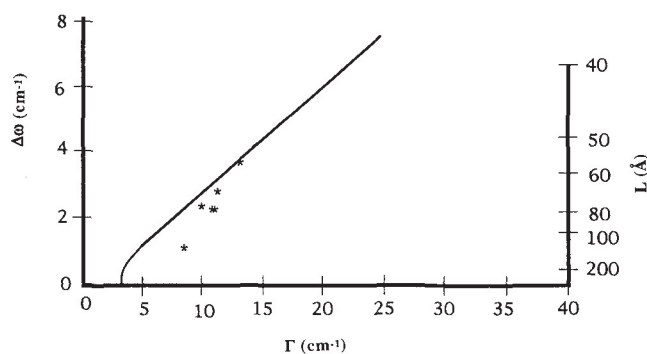


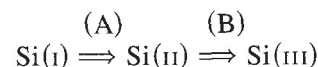
FIG. 5. Calculated relationship between linewidth Γ , frequency shift $\Delta\omega$, and grain size L using a Gaussian weighting function and assuming a spherical microcrystalline domain. Experimental data points extracted from the Raman peaks of crystalline components shown in Fig. 4 are indicated by an asterisk.

metal oxides.³⁰ For milled SiO_2 , a partial transformation of the crystalline phase to an amorphous phase has been obtained.³¹ It is believed that the mechanochemical equilibrium of the two polymorphs is a function of the pressure-temperature conditions and grinding regime.³² Additionally, pressure-induced amorphization has been observed for C, Si, Ge, and many other alloy systems.³² For the SPEX mill, it is estimated that the obtainable pressure ranges from 3.30 GPa to 6.18 GPa.³³ The ball compression and its subsequent relaxation, i.e., loading and unloading time in the Spex mill, is estimated to be 10^{-2} ms.³³ At this rapid unloading rate it is possible

that the high-pressure, crystalline form of Si cannot transform back fast enough to the equilibrium structure such that the amorphous phase forms metastably. It is also possible that during the ball-powder-ball or ball-powder-wall collisions the local pressure exceeds the metastable extension of the liquidus curve on the T - P phase diagram; thus, the amorphous phase is formed directly on compression and persists on separation of ball and powder because of insufficient thermal energy to allow rearrangement back to the diamond cubic form. These two similar amorphization mechanisms have been proposed for the indentation-induced amorphization of single-crystal Si and Ge.³⁴ The ball-powder-ball and ball-powder-wall collisions in the Spex mill can exert a pressure to the powder that is of the same magnitude as the pressure produced by indentation. As for the unloading time, the unloading occurs in about 30 ms for the indentation process while it occurs in about 10^{-2} ms for the milling-induced collision process. Therefore, the first mechanism may be possible for the partial amorphization of Si by ball milling. As for the second mechanism, the calculated T - P diagram shows that at room temperature a pressure of about 18 GPa would be required for such a direct crystal-to-amorphous transformation.³⁵ If one considers the point contacts between particles when pressure is first applied, the resulting effective pressure value is infinitely high.³⁶ Thus, the second mechanism is also possible for the milling-induced amorphization at the particle surfaces. A possible verification for this mechanism is that the relatively large volume fraction of amorphous phase near the particle surface regions, as shown in Fig. 2(b), may result from the high pressure produced by the instantaneous point contacts between particles.

2. Crystallite-refinement-induced amorphization

A mechanism for crystallite refinement of Si and Ge during ball milling has been proposed recently.³⁷ It is believed that the refinement is induced by the mechanical shocks, not during the direct loading pressure (A), but during the unloading (B) following the mechanisms:



where Si(II) exhibiting the βSn structure shows a volume decrease of 22% [compared to Si(I)], and Si(III) a decrease of 8% [compared to Si(I)]. The I to II stages have been found to occur at 11.3 GPa, and the II to III transition at 7.5–9 GPa. As the Si(III) exhibits a larger structural volume than the Si(II), a kind of explosion occurs during the unloading process, leading to a refinement of the grain size.

In the present discussion, we try to answer this question: why does the refinement of grain size result in

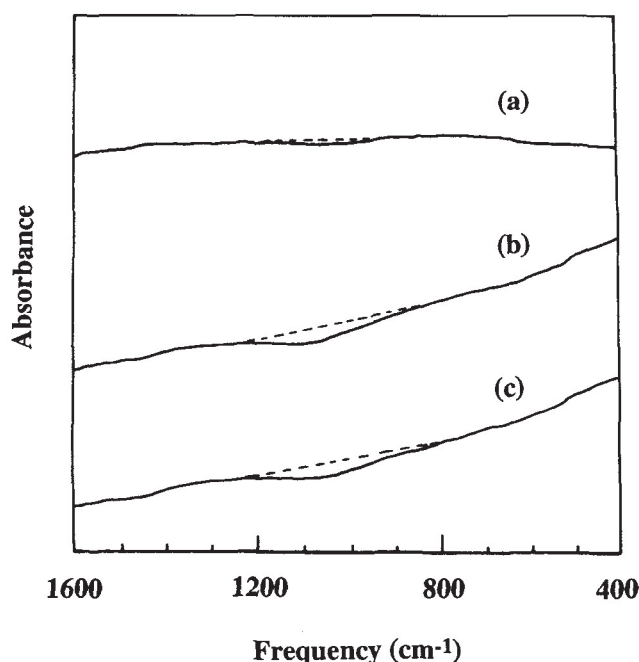


FIG. 6. Infrared spectra of polycrystalline Si powder after (a) 0 h, (b) 3 h, and (c) 38 h of milling.

amorphization from the viewpoint of thermodynamics? Thermodynamically, the crystal-to-amorphous transition in Si induced by ball milling is the increase in free energy of crystalline Si probably due to the energy of nanocrystalline grain boundaries.

When a small "critical" grain size has been attained such that the free energy of amorphous Si is reached, the transformation occurs. This critical grain size was estimated to be 3 nm³⁸ or 8 nm.⁹ That partial amorphization occurs in Si may be related to the fact that a distribution of nanocrystalline grain diameters exists after milling and only those regions with grains ≤ 3 nm can transform. This suggestion is illustrated in Fig. 7 where the estimated grain boundary energy as a function of grain size is plotted along with the crystallization energy. The data plotted in this figure were estimated in the following manner. The crystallization free energy for amorphous-crystalline Si was taken from Ref. 17. The total grain boundary energy was calculated by taking cubical grains to obtain the total grain boundary area and using values of the specific grain boundary energy calculated by Phillpot and Wolf³⁹ for different misorientation angles and (111), (110), and (001) grain boundary planes. These values range from 0.64 J/m² to 1.46 J/m² with an average value of 1.1 J/m². Grain size is given as $1.209 \times \text{cube side}$.⁴⁰ According to Fig. 7, the critical grain size for amorphization is determined to be about 3 to 5 nm. The critical grain size of ≤ 3 nm is consistent with the smallest crystalline domains observed in the HREM images of Fig. 2(b).

B. Structure and thermal properties of milled polycrystalline Si

As shown by the present investigations, a mixture of amorphous and nanocrystalline Si was prepared by ball milling of polycrystalline elemental Si powder. Dislocations, twins, and stacking faults, which are typically defects in conventional coarse-grained polycrystals, exist in the milled Si. The distribution of the amorphous phase formed by ball milling is not homogeneous. In regions near the surface of the milled particles, the volume fraction of amorphous phase is comparable with that of the crystalline phase in contrast to the average volume fraction of the amorphous phase of about 15%. This may be due to the higher density of defects created by milling-induced plastic deformation and/or the higher oxygen content in the regions near the particle surface.

The thermal stability and structure of milling-induced amorphous Si seem to be very similar to those of amorphous Si prepared by other methods. The amorphous Si formed by ball milling exhibits a comparable crystallization temperature and crystallization activation energy with those for amorphous Si formed by ion implantation or chemical vapor deposition. As

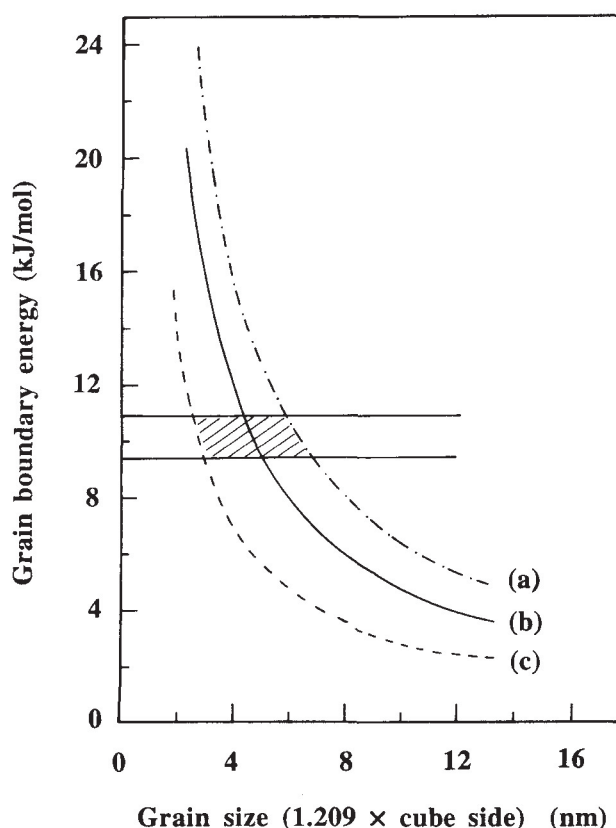


FIG. 7. Estimated grain boundary energy as a function of grain size. The horizontal lines show the position of crystallization energy. The grain boundary energy was taken as 1.46, 1.1, and 0.64 J/m² for curves (a), (b), and (c), respectively.

for the structure, the positions of the peak maximum and FWHM related to the amorphous components in the Raman spectra of ball-milled Si are also similar to those of ion-implanted or evaporated amorphous Si.^{26,27} It is believed that the structure of amorphous Si is of a covalently bonded continuous random network.⁴¹ On the average, the angles between bonds for amorphous Si diverge 7° to 12° from the ideal tetrahedral angle in perfect crystalline Si.^{41,42} Moreover, it has been shown by modeling studies⁴² that it is impossible to construct any random network for amorphous Si if the root-mean-square bond-angle distortion, $\Delta\Theta_b$, ranges from 0° to 6.6°. This provides a fundamental distinction between amorphous Si and crystalline Si. $\Delta\Theta_b$ can be calculated by the expression⁴⁴

$$\Delta\Theta_b \cong (\text{FWHM}/2 - 7.5)/3, \quad (4)$$

where FWHM/2 is the half width of the transverse optic (TO) peak in the Raman spectra. Accordingly, the $\Delta\Theta_b$ value is determined to be 10.4°, 10.0°, 9.9°, and 9.8° for the amorphous Si in samples Si-3 h, Si-38 h, Si-3 h annealed at 390 °C, and Si-38 h annealed at 390 °C, respectively. All of these $\Delta\Theta_b$ values indicate

the existence of the structure of amorphous Si in ball-milled Si and the similarity in structure of the amorphous Si formed by ball milling to that obtained by vacuum evaporation or ion-implantation.⁴⁵ For annealed samples Si-3 h and Si-38 h at 725 °C, the $\Delta\Theta_b$ values are 5.7° and 6.25°, indicating the disappearance of the amorphous structure after annealing at 725 °C, giving further verification that the sharp DSC peak shown in Fig. 3 is due to the crystallization of the amorphous phase formed by ball milling.

The volume fraction of the amorphous phase estimated from the DSC peaks is much less than that from the RS peaks. This is because the so-called amorphous component estimated from RS signals includes the disordered atoms both in amorphous regions and in grain boundaries.⁴⁶ The atoms in grain boundaries can be comparable in number with those in the crystals when the grain size is below 10 nm.⁵ Thus, the atom percent in grain boundaries is equal to the difference between the “amorphous” fraction estimated from the RS signal and that from the DSC signal if the fraction of Si powder surfaces is neglected. Accordingly, the atom fraction in grain boundaries for samples Si-3 h and Si-38 h is estimated to be 18% and 23%, respectively. Additionally, the atom fraction in grain boundaries can also be estimated from the corresponding relationship between atomic grain boundary fraction and grain size.⁵ If the average grain boundary thickness is taken as twice that of the Si(111) atomic plane width, i.e., 0.63 nm, and the average grain size is taken as the average value of the grain size estimated from XRD patterns and Raman spectra, i.e., 10.5 nm for sample Si-3 h and 8 nm for sample Si-38 h, then the atom fraction in grain boundaries is estimated to be 17% and 22% for sample Si-3 h and sample Si-38 h, respectively. These grain boundary fractions are in good agreement with those estimated from Raman spectra and DSC signals.

Various values for the crystallization temperature of amorphous Si have been reported.^{15,16,20} In the present work amorphous Si formed by ball milling has similar (but lower) crystallization temperatures compared with those of amorphous Si prepared by ion implantation. This may be related to the existence of nanocrystalline Si acting as “heterogeneous” nuclei for crystallization. Thus, the crystallization temperature is decreased compared with those of completely amorphous Si. The amorphous Si formed by ball milling, however, exhibits similar crystallization activation energy to that prepared by ion implantation.^{20,22,23} This indicates further the similarity in structure of the amorphous Si prepared by ball milling and ion implantation. Most of the amorphous Si in our milled Si sample should be amorphous elemental Si without combined oxygen because amorphous SiO₂, if it existed, should exhibit a crystallization temperature located in the region from 800 to 870 °C.¹⁰ A possible

explanation for the reported abnormally high crystallization temperature and activation energy reported by Gaffet and Harmelin⁹ may be the oxygen contamination after ball milling up to 70 h, as suggested by Bokhonov *et al.*¹⁰ However, the oxygen content in this ball milled Si has not been reported.⁹

V. SUMMARY

Two phase amorphous plus nanocrystalline Si has been produced by ball milling of polycrystalline elemental Si. Amorphous elemental Si without combined oxygen can be obtained by ball milling. The nanocrystals contain defects such as dislocations, twins, and stacking faults. The amorphous Si formed by ball milling exhibits similar (but lower) crystallization temperatures and very similar crystallization activation energy values compared with those of amorphous Si prepared by ion implantation. Structurally, the amorphous Si prepared by ball milling is similar to that obtained by ion implantation or chemical vapor deposition. Two possible amorphization mechanisms, i.e., pressure-induced amorphization and crystallite-refinement-induced amorphization, were proposed for the amorphization of Si induced by ball milling.

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