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The stages of formation of a solid solution during the mechanical alloying of Si and Ge

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Abstract

The formation of a solid solution during the mechanical alloying (MA) of Si and Ge was studied using electron microscopy and X-ray diffraction. The process occurs via the formation of aggregates in which, under the action of plastic deformation, the mutual diffusion of Si and Ge proceeds to form the solid solution $Si_{1-x}Ge_x$. According to our data, the observed partial amorphization of the components during MA is due to the formation of amorphous SiO and $Si_{1-x}Ge_xO$ oxides, structurally similar to amorphous Si.

1. Introduction

The methods of mechanical alloying (MA) and mechanical grinding (MG) of solids have recently been widely used for the synthesis of crystalline and amorphous intermetallics [1]. The interaction of two brittle substances during MA has not been studied in detail and the mechanism is still unknown. An example is the formation of a solid solution during the MA of Si and Ge. In addition to theoretical interest, the system is of practical significance because of the peculiar physicochemical properties of the solid solution of Si and Ge and its application in microelectronics.

The MA of Si and Ge has been studied previously [2–4]. It has been shown [2] that during MA Si and Ge form a continuous series of solid solutions. Davis and Koch [2] have revealed a deviation in the relationship between the crystalline lattice parameter and the concentration of the components (Vegard's law) for the solid solution Si–A%Ge at $A > 28\%$.

In addition to solid solutions, insignificant amounts of SiO_2 and GeO have been found during MA.

Gaffet and coworkers [3, 4] have revealed the crystalline–amorphous phase transition during the MA of Si and Ge. In this case, the amorphization process is characteristic of both pure Si and Ge and of the solid solution.

In the present work, the aim was twofold: (1) to study the stages involved in the formation of the solid solution during the MA of Si and Ge in high-energy activators; (2) to elucidate the possible causes leading to the transition of crystalline Si and Ge into the amorphous state during MA.

2. Experimental details

Si (purity 99.999%) and Ge (purity 99.99%) were used as starting components for the preparation of the solid Si–Ge solution. MA was carried out in a centrifugal planetary ball mill with an acceleration of 600 m s^{-2} and in stainless steel vials filled with argon or air. X-ray studies were conducted on a diffractometer using Co Kα radiation. Electron microscopy was performed on a JEM-2000FX2 microscope at an accelerating voltage of 200 kV.

3. Results and discussion

The formation of the solid solution during the MA of Si and Ge is observed throughout the concentration range under study after treatment for 20 min. This time is an order of magnitude smaller in comparison with the data obtained in refs. 2–4, which is due to the higher efficiency of the activator used in our work. Nevertheless, the results obtained agree well with the results of refs. 2–4. As the time of MA increases, the Si and Ge reflections possessing the same indices merge. This indicates the beginning of the formation of a solid solution and the diffusion of both Si into Ge and Ge into Si. In this case, the Si and Ge reflections are broadened, and after mechanical treatment for 8 min

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the X-ray diffraction patterns reveal an insignificant increase in the background between the (220) and (311) reflections (Fig. 1), which indicates a partial amorphization of the components. After mechanical treatment for 20 min, the X-ray diffraction patterns show only reflections corresponding to the Si–Ge solid solution and a small amount of an amorphous phase which manifests itself by an increase in the background between the (220) and (311) reflections. The dependence of the parameter of the crystalline lattice of the Si–Ge solid solution on the concentration of the components, calculated from the X-ray data (Fig. 2), is linear, which is consistent with Vegard's law. The violation of this law found in ref. 2 appears to be due to the difference between the stoichiometry of the Si–Ge solid solution and the ratio of the powders initially used.

Electron microscopy studies of the MA of Si and Ge show that the initial stages of treatment of the powders involve grinding and aggregation (Fig. 3(A)). The electron patterns of the aggregates formed after mechanical treatment for 4 min (Fig. 3(B) show reflections of crystalline Si and Ge). Increasing the time of MA leads to a decrease in the size of the aggregates. In this case, part of the surface of the crystalline particles is coated with an amorphous layer several tens of angströms thick. After mechanical treatment for 20 min, the electron patterns of the aggregates show only reflections of the Si–A%Ge solid solution and the surface of the aggregate is completely coated with a thin amorphous layer (Figs. 4(A) and 4(B)).

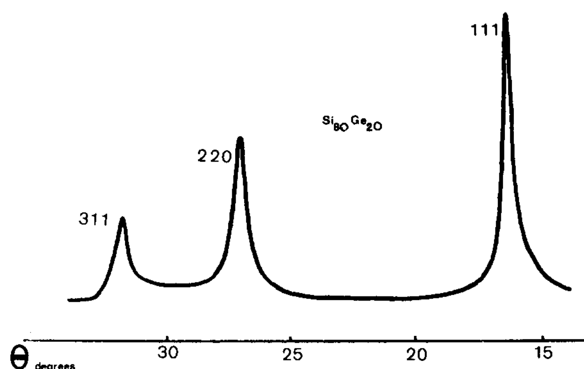


Fig. 1. X-ray pattern of the solid solution $Si_{80}Ge_{20}$ after mechanical treatment for 20 min. Partial amorphization is observed.

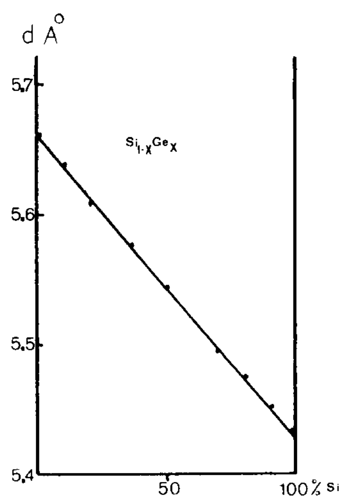


Fig. 2. Dependence of the crystalline lattice parameter of the $Si_{1-x}Ge_x$ solid solution on the concentration of the components.

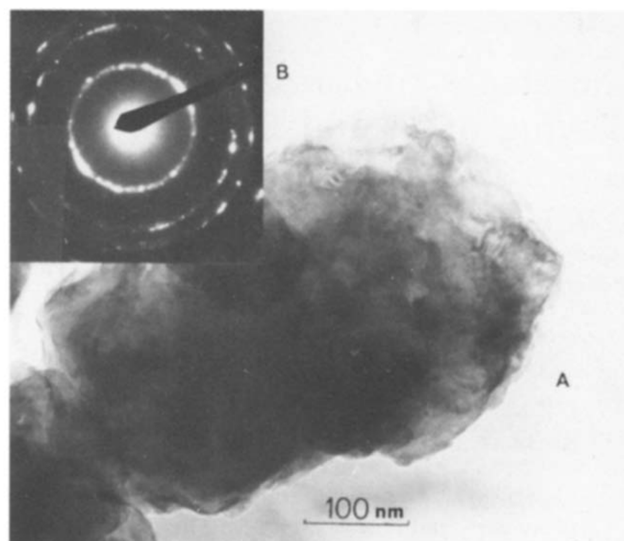


Fig. 3. Electron micrograph (A) and the corresponding electron pattern (B) from an aggregate formed after mechanical treatment of Si and Ge for 4 min.

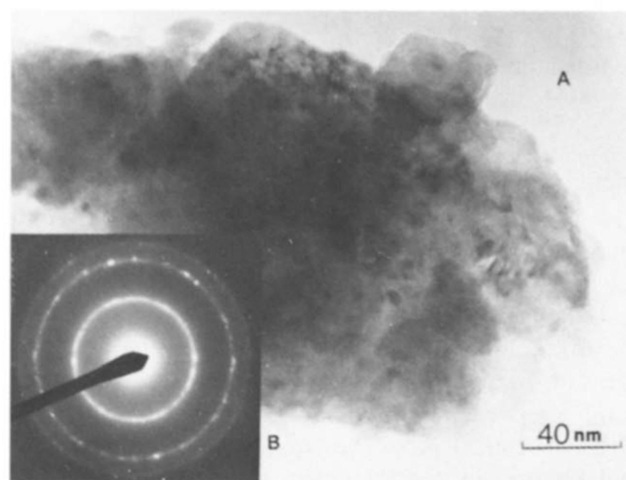


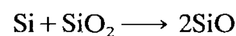
Fig. 4. Electron micrograph (A) and electron pattern (B) from an aggregate obtained after mechanical treatment of Si and Ge for 20 min. The electron pattern shows reflections of only the $Si_{1-x}Ge_x$ solid solution.

The formation of the amorphous layer on the surface of the crystalline particles of the solid solution may be due to a number of causes: (1) the transition of part of the Si or Ge crystals into the amorphous state under

the action of plastic deformation or destruction on mechanical treatment; (2) amorphization associated with oxidation of the crystal surface.

In refs. 3 and 4, the transition from the crystalline into the amorphous state is attributed to the causes mentioned in (1), *i.e.* during mechanical treatment the particles decrease in size and the lattice parameter increases, which leads to the destabilization of the Si and Ge structure. In our opinion, however, the oxidation process may play a significant role in the amorphization during MA. Such a suggestion is based on a number of experimental facts obtained by us or given in the literature. The amorphization rate depends on the atmosphere under which the MA is carried out. The presence of oxygen in the vial increases the concentration of the amorphous phase during the MA of Si and Ge in contrast with an inert atmosphere. It is known from the literature [5] that even the conventional methods of preparation of amorphous Si and Ge (sublimation in vacuum or argon; electrolytic deposition or glow discharge deposition) yield samples with an appreciable oxygen content (up to 7%). According to the data of refs. 3 and 4, the temperature of the transition from the amorphous to the crystalline state, determined for Si by the mechanochemical method, is 800 °C. However, the temperature of crystallization of amorphous silicon films several micrometres thick and not containing oxygen lies in the range 400–500 °C, according to the data given in ref. 5. Such a substantial difference in the crystallization temperatures cannot be explained simply in terms of the method of preparation of the amorphous phase. Moreover, in ref. 2, the formation of SiO_2 and GeO was detected after several hours of MA of Si and Ge. Although the reaction volume was initially filled with argon, oxidation during MA after long times of treatment may be observed due to the poor tightness of the vial or the presence of oxygen in the inert gas.

To verify this hypothesis, we deliberately added 20% of SiO_2 to pure Si, Ge and their solid solution. In this case, a marked change in the structure of such mixtures was observed in the X-ray and electron patterns even after 10 min of MA. The sequence of stages in these systems is the same and is characterized at the initial stage (approximately 30 min) by the transition of quartz from the crystalline into the amorphous state: the first amorphous halo is located near the $(101)_{SiO_2}$ reflection. An increase in the time of MA to 1.5 h leads to a practically complete amorphization of SiO_2 and Si. The first amorphous halo is located near the $(111)_{Si}$ reflection and the second between the $(220)_{Si}$ and $(311)_{Si}$ reflections (Fig. 5). The X-ray patterns show the complete absence not only of reflections of crystalline α-quartz but also of an amorphous phase which could form during mechanical treatment. After mechanical treatment, the substance acquires a brown colour characteristic of the suboxide SiO. Electron microscopy studies confirm the formation of amorphous particles several thousands of angströms in size. The electron patterns of such particles coincide with the known data on amorphous Si and Ge obtained by the thermal deposition method [6, 7] (Fig. 6). In our case, however, it may be argued that the MA of Si–SiO_2 leads to the formation of the amorphous silicon suboxide SiO and $Si_{1-x}Ge_xO$ by the reaction



$$Si + SiO_2 \longrightarrow 2SiO$$

The differential thermal analysis (DTA) curves corresponding to the Si–SiO_2 alloys and Si–20%Ge solid solution, obtained using MA, are presented in Fig. 7. As can be seen from this figure, an exothermic peak corresponding to the phase transition from the amorphous to the crystalline phase is located in the region 800–870 °C for all of these alloys. This indicates that the formation of the amorphous phase during the MA of pure Si and Ge is also associated with the oxidation process. The annealing of all the above samples at 900

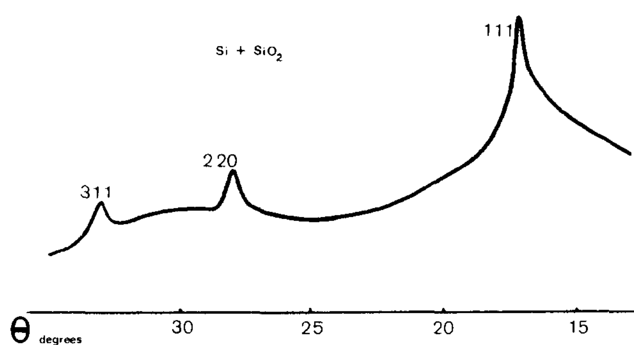


Fig. 5. X-ray pattern of an amorphous phase formed after 1.5 h of MA of Si–20%SiO_2.

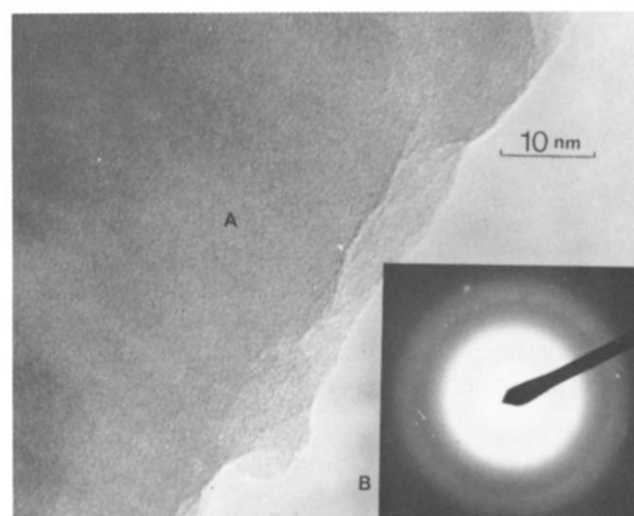


Fig. 6. Electron micrograph (A) and electron pattern (B) of an amorphous particle formed during MA of Si and SiO_2.

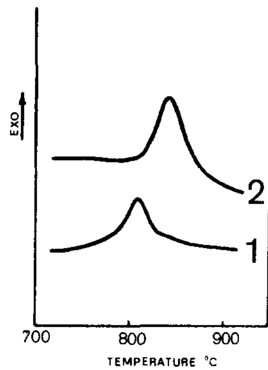


Fig. 7. DTA curves for the $Si_{80}Ge_{20}$ solid solution (1) and SiO (2) obtained using MA.

°C leads to the disappearance of the amorphous phase. The X-ray patterns show only the reflections of crystalline Si(SiO) which cannot be practically separated because of their complete alignment.

Thus the study of the MA of Si and Ge shows that the process proceeds through the aggregation stage. The formation of an amorphous layer on the surface of crystalline particles probably favours the aggregation process. The formation of the Si–A%Ge solid solution proceeds by mutual diffusion of Si and Ge in the aggregate under the action of plastic deformation.

According to our data, the crystalline–amorphous phase transition during the MG and MA of Si and Ge, associated by Gaffet and coworkers [3, 4] with the partial amorphization of pure Si, Ge and their solid solution, may be attributed to the amorphization of the oxides SiO and $Si_{1-x}Ge_xO$ which are similar in structure to Si. During the course of MG or MA, Si and Ge interact with oxygen to form SiO_2 and the MA of Si and SiO_2 or of $Si_{1-x}Ge_x$ and SiO_2 takes place, resulting in the formation of amorphous SiO or $Si_{1-x}Ge_xO$.

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