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Journal of Alloys and Compounds 312 (2000) 238–250

Journal of
ALLOYS
AND COMPOUNDS

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In situ investigation of stage of the formation of eutectic alloys in Si–Au and Si–Al systems

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Received 22 May 2000; accepted 15 August 2000

Abstract

The in situ electron microscopic investigations of the formation of eutectic alloys in the systems: amorphous Si/particle Au, amorphous Si/particle Al showed that the formation of eutectics is preceded by metal diffusion into amorphous silicon with the formation of metastable amorphous metal silicide. Supersaturation and decomposition of the metastable amorphous metal silicide leads to the evolution of polycrystal silicon. Morphological characteristics of the liquid eutectic formation in the systems crystalline (100)Si/particle Au and crystalline (100)Si/particle Al are similar to the well known morphological characteristics of the formation of etch pits in crystals. For the systems crystalline (100)Si/particle Au, an oriented formation of the liquid eutectic alloy is observed. The growth of the eutectic melt during the annealing of the system crystalline (100)Si/particle Al takes place isotropically. The crystallization of liquid eutectic alloy leads to toptaxial evolution of gold silicide islands at the interface: crystal eutectics–single crystal silicon. © 2000 Published by Elsevier Science B.V.

Keywords: Interface reaction; Eutectic formation; Transmission electron microscopy (TEM); Metastable compounds; Alloys

1. Introduction

Among the impressive variety phase diagrams of binary systems, the most simple one is perhaps the phase diagram of the eutectic type in which any intermetallic phases are absent and only solid components of definite composition are observed to pass jointly to the liquid state. However, in spite of the obvious simplicity of these phase diagrams, the formation mechanism and structure of eutectic alloys attract increasing attention. It should be noted that, while the structure of crystal eutectic alloys has been thoroughly studied experimentally, the structure of liquid eutectics is less investigated. Moreover, the question concerning the mechanism of liquid eutectic formation is still open to discussion. This is due to the difficulties connected with obtaining experimental data on the structure of the interface during the formation of eutectic alloy directly at the moment when the conjugated solid components pass from the solid state to the liquid.

At present we can stress at least two basic mechanisms of eutectic alloy formation [1]. According to the first one, the formation of eutectic alloy is preceded by the forma-

tion of intermediate layer of supersaturated solid solution accompanied by the increasing of defects concentration into these layer and increase of the free energy of the system which is the reason why eutectic systems are easily melting. According to the second mechanism which is referred to as «the adhesion theory of contact melting» [1], the interaction of surface atoms occurs in micro-regions of physical contact between the conjugated crystal phases, and the transition epitaxial zone (without formation of solid solution) are formed. In the opinion of the authors developing this concept [1], the formation of these transition epitaxial zones should lead to the decrease of misfit (differences in lattices parameters between solid phases at the interface region), to the appearance of stress at the interface, and to the increase of the elastic energy of the interface. Besides, the formation of the epitaxial zone leads to weakening of the bonds in the surface layers of contacting crystals which provides the decrease of temperature at which the system passes into the liquid state.

One of the most interesting eutectics, both from the scientific and practical points of view, are the systems: gold–silicon and aluminum–silicon. This is due to negative enthalpy of components mixing in this system which, in the opinion of some authors, implies the formation of a chemical compound in liquid phase [1].

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Earlier studies of quenched thin amorphous films with composition close to eutectics in the Au–Si system by means of Auger electron spectroscopy [2] revealed a series of rather interesting facts that characterize the transition of silicon into metal state. A similar transition of silicon into metal state was also observed when metals were added (silver or gold). According to the data presented in [2], the transition of semiconductor element in metal state is due to the change of silicon coordination number in the metastable amorphous alloy which leads to the change of the electron state of valence electrons of silicon. This causes the appearance of two maxima in Auger spectra at 90 and 95 eV, unlike the peak at 92 eV which is characteristic of semiconductor silicon.

Similar results were obtained in the studies of the Au–Si system when a thin gold film was deposited onto the pure surface of single crystal silicon at room temperature [3]. Since the adhesion of gold film formed on the silicon surface was very high, the authors assumed the formation of some transition region till the formation of a chemical compound at the interface. They concluded that the interface layer was due to diffusion and contained up to 20–45 gold monolayers (depending on the orientation of silicon crystal which was (100) or (110)). The possibility of the formation of quasi-compounds with composition close to the eutectics was also concluded.

Problems related to the changes in the structure of interface boundary during thermal treatment in the system: deposited gold film–single crystal silicon are considered in [4,5]. It was found that the formation of the diffusion interface between gold and silicon is observed much below the melting point of eutectics at temperatures within 150–300°C. Since the formation of silicon oxide took place on the surface of the deposited gold film during low-temperature annealing, it was concluded that silicon diffusion through gold layer is predominant. Besides, it was demonstrated that the growth rate of silicon oxide layer on the surface of gold film deposited onto single crystal silicon (110) surface was five times higher than on the (111) surface.

Besides the problem connected with the interface structure during the formation of eutectic alloys, substantial attention was paid also to the structure of liquid eutectics themselves. The literature data on the structure of eutectic melts in the system Au–Si are contradictory. For instance, an intermediate metastable phase was observed in the experiments on quenching of melts. The formation of a usual two-phase structure was observed when gold melt was quenched with 20% silicon [6]. An increase of the melt temperature to 600°C before quenching allowed to observe a metastable compound Au_4Si . It was assumed that interatomic interaction and the structure of the melt under consideration are substantially changed within temperature range 400–600°C, micro-layering to the region of the atoms of one kind (gold and silicon) is transformed into ordering of the type of a chemical compound.

According to these data, heating to about 1000°C caused chaotic distribution of silicon and gold atoms.

The authors of [7] did not observe the formation of a chemical compound in the melts in the system Au–30.9%Si, and concluded that the distribution of silicon and gold atoms in the melt was chaotic at 380–650°C.

Many works deal with the structure of liquid alloys in the system Al–Si but the data obtained, as well as their interpretation are rather contradictory [1]. On the one hand, a series of thermodynamic characteristics of the system Al–Si was the evidence of the predominant interaction between the atoms of different kinds in the melt; on the other hand, many works on rapid quenching of melts did not report the formation of intermediate metastable states. For example, when aluminium melts were quenched with 18–39% silicon (cooling rate 100°C/s) and the melt with 25% silicon (cooling rate 100°C/s) [1] the structure of quenched samples was a two-phase system composed of a solid solution based on aluminum and silicon particles. Substantially different picture was observed in [8] for quenched melts of aluminum and silicon with 20.5% silicon. At a quenching temperature of 710°C weak X-ray reflections of the unknown phase were observed. Since the position of X-ray reflections was changed from some experiments to other, the authors did not succeed in identifying the formed metastable phase. The authors assumed that at silicon concentration of 15–20% in pre-eutectic and eutectic melts, the formation of micro-regions with the structure and composition similar to aluminum silicide takes place. However, a direct X-ray investigation of liquid eutectic alloys did not confirm the formation of micro-regions with the structure and composition of aluminum silicide [9]. According to the opinion of the authors, the regions of statistical non-ordered distribution of Al and Si atoms exist in the eutectic melt.

The analysis of literature data allows us to conclude that by present the question remains which one of the above theories provides a reliable description of the stage sequence in the formation of eutectics, which is the structure of the interface of the liquid eutectic phase being formed, and what is the structure of liquid eutectics itself?

In the present study we have made an attempt to model directly in situ using electron microscope the formation of eutectic melts in the systems gold–silicon and aluminum–silicon. In our opinion, these in situ experiments allow to obtain additional data that will provide progress in the understanding of the formation and structure of eutectic alloys.

2. Experimental

In-situ electron microscopic studies were performed using transmission and scanning electron microscope JEM-2000 FX II equipped with a special holder to heat the

samples (EM-SHH4). The temperature was measured by Pt–Pt,Rh(13%) thermocouple with accuracy $\pm 10^\circ\text{C}$.

Single crystal silicon films (1000–2000 Å) were prepared by chemical etching of (100) single crystal silicon plates by 98% HNO_3 , 40% HF in a ratio 1:1.

A 1500 Å thick amorphous Si layer was deposited on the surface of (100) NaCl crystals in vacuum chamber (pressure $\sim 2 \times 10^{-7}$ Torr during evaporation) by electron gun evaporation. Transmission electron microscopy samples were prepared by floating off the NaCl substrate in de-ionized water and picking the film up on copper grids.

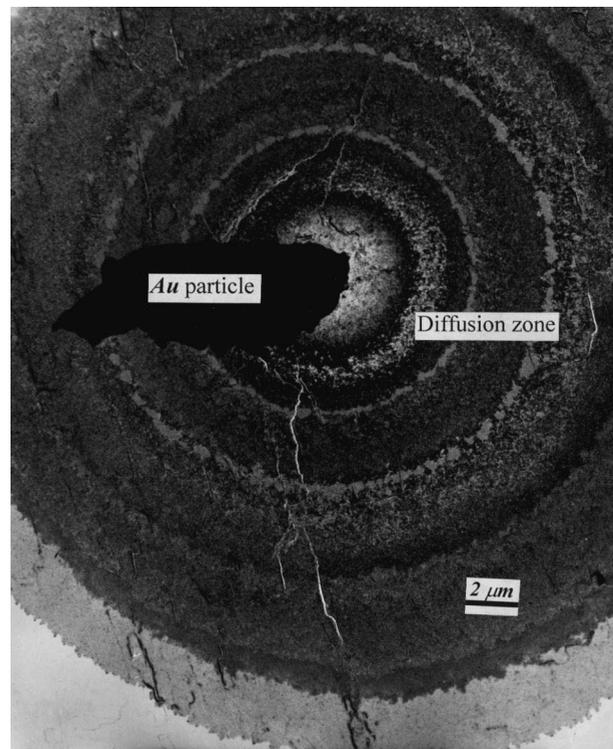
Before in-situ experiments, in order to create reaction couples, fine particles of gold or aluminum were deposited onto the surface of silicon thin films or single crystal foils. In some cases metal particles were heated locally by focusing a high-intensity electron beam (beam current 10^{-1} – 10^{-2} A/cm²) on their surface in order to provide more tight contact between the silicon film (foil) and the particle. We used the EF-4 electron microscope (Carl Zeiss Jena) for this purpose.

Along with the investigation of the interaction of single-crystal and amorphous silicon with gold particles, we studied morphological and structural changes during the annealing of silicon particles deposited onto the surface of single-crystal gold film (up to 2000 Å thick). The sample was prepared by thermal spraying in vacuum (at a pressure of $\sim 2 \times 10^{-7}$ Torr during evaporation) on fresh surface of (100) NaCl crystals heated to 400°C.

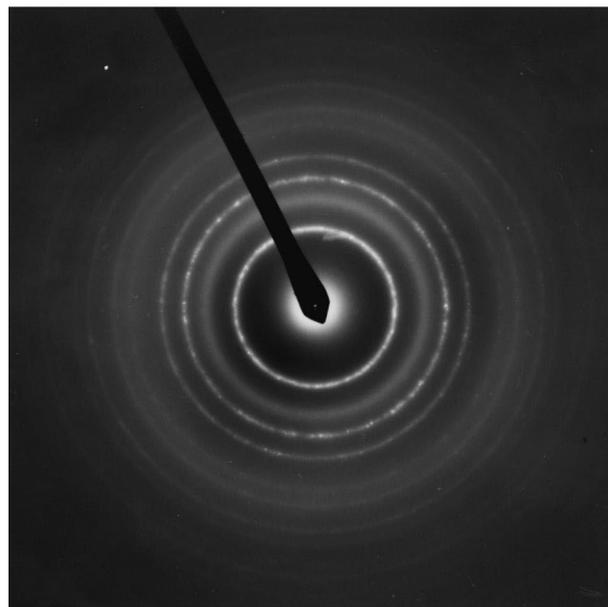
3. Results

3.1. Changes of morphological and structural characteristics during the annealing of amorphous silicon film with gold particle

Our investigations of the changes of morphological and structural characteristics during in situ annealing of the amorphous silicon film with gold particle showed that heating method has a substantial impact on the character of solid reaction products evolution. For example, if the system amorphous Si/particle Au is heated with the help of electron beam of the microscope (beam current 10^{-1} – 10^{-2} A/cm²), the following changes are observed in morphology and structure of the interacting system. First, during heating of system by electronic beam of small intensity (10^{-2} A/cm²), a rapid propagation of the interface from gold particle on the surface into the amorphous silicon film is observed. Morphological characteristics of the product layer formed involve the formation of periodic concentric layers of different intensity (Fig. 1a). The interaction started at temperatures below gold melting point because no morphological changes were observed in gold particle which remained solid. Diffraction characteristics of the layers of products formed are characterized by the presence of ring-like reflections of crystal silicon and a



(a)



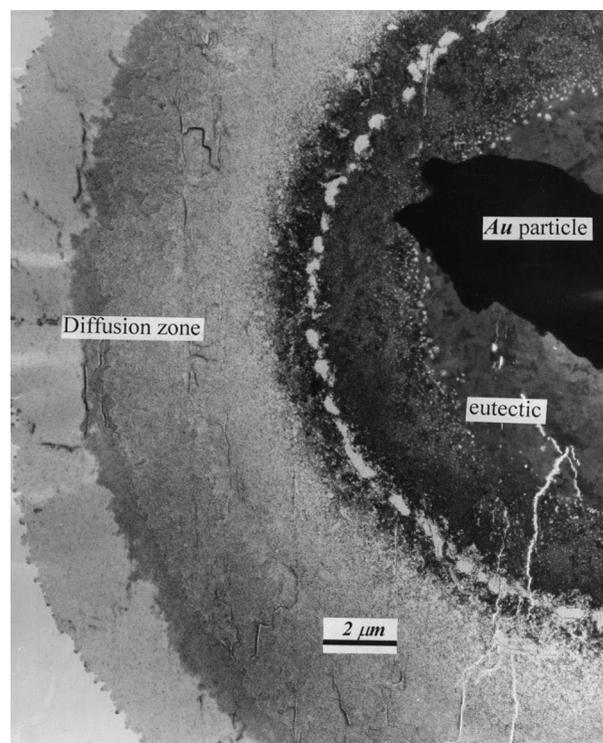
(b)

Fig. 1. (a) Morphological characteristics of the diffusion zone of the products of interaction between gold particle and amorphous silicon film formed during the heating with electron beam. The formation of periodic concentric layers of the product of different intensity are observed. (b) SAD pattern from the diffusion zone (Fig. 1) of the products of interaction between gold particle and amorphous silicon film. Diffraction characteristics of the layers of products formed are characterized by the presence of ring-like reflections of crystal silicon and a diffuse halo with the maximum intensity corresponding to the interplanar distance $d = 2.45$ Å.

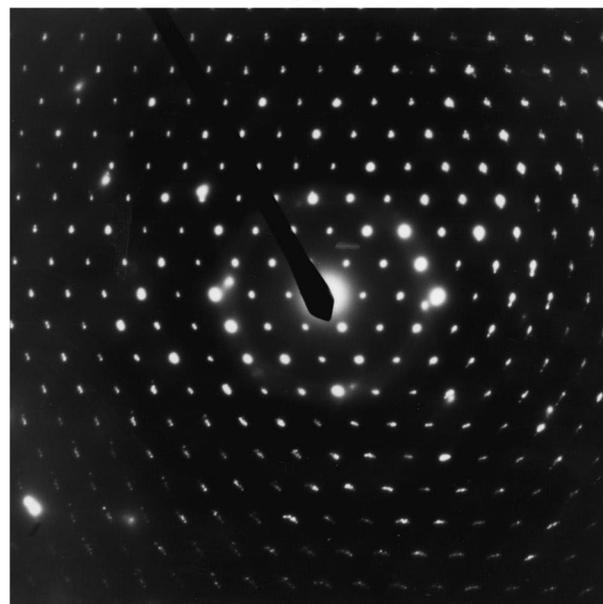
diffuse halo with the maximum intensity corresponding to the interplanar distance $d=2.45\text{Å}$ (Fig. 1b). If the system amorphous Si/particle Au is heated at high electron beam intensity (10^{-2} A/cm^2), then the propagation of the reaction front also occurs into the amorphous silicon with the formation of concentric product layers and with the formation of the eutectic alloy Si–Au in the vicinity of gold particle (Fig. 2a). Similar to the case of heating with low-intensity electron beam, concentric zones are mixtures of polycrystal silicon and amorphous substance. Morphological characteristics of the eutectics decomposed after cooling (sharp decrease of electron beam intensity) reveal the presence of dendrite silicon crystals distributed over polycrystal gold. After cooling the sample, in local regions of crystallized eutectics, along with the expected and predicted (according to the phase diagram) gold and silicon phases, a crystal metastable compound of gold and silicon is observed. This is confirmed by electron diffraction data (Fig. 2b) containing the reflections with much larger lattice parameters than those expected for silicon and gold.

In situ investigation of annealing of the system amorphous Si/particle Au in a special holder for electron microscopic sample heating (in the case under consideration the process is more isothermal by its character) showed some general regularities of the interaction, as well as some differences when the system is heated with an electron beam. It should be noted that structural and morphological changes in the system amorphous Si/particle Au during isothermal annealing are observed at temperatures much below the eutectic melting point (375°C). For example, at a temperature as low as 300°C we observe the formation and propagation of the reaction front into the silicon amorphous film (Fig. 3). Unlike the case of electron beam heating of amorphous Si/particle Au, no formation of concentric rings of different intensity is observed during isothermal annealing. In the case under consideration, the formation of a uniform product layer occurs. Diffraction characteristics of this product, similar to electron beam heating, exhibit the presence of polycrystal silicon and amorphous compound with diffuse halo, its maximum intensity corresponding to the interplanar distance of $d=2.45\text{Å}$ (electron diffraction patterns are identical to that presented in Fig. 1b).

An increase in annealing temperature of the system amorphous Si/particle Au above the eutectic melting point is characterized both by the propagation of the amorphous silicon crystallization zone and the formation of amorphous compound, and by the formation of eutectic alloy near gold particle (Fig. 4a). Annealing and the formation of eutectic alloy are accompanied by a substantial decrease of the size of gold particle with a simultaneous increase of the zone of liquid eutectic alloy. Diffraction patterns of the liquid eutectic alloy is a set of diffuse rings with maximum of interplanar distances $d=2.45\text{Å}$ and $d=1.15\text{Å}$ (Fig. 4b). Cooling of the eutectic alloy leads to dendrite crystallization of silicon. Its crystals grow in polycrystal



(a)



(b)

Fig. 2. (a) Electron microphotograph of the diffusion and eutectic zones formed during the heating with electron beam of the system-gold particle/amorphous silicon film. (b) SAD pattern of metastable crystal gold silicide formed after cooling of the eutectic Au–Si alloy. SAD pattern containing the reflections with much larger lattice parameters than those expected for pure silicon and pure gold.

gold matrix (Fig. 5). Unlike the crystallization of eutectic alloy obtained by electron beam heating of the system amorphous Si/particle Au, the crystallization of the eutec-

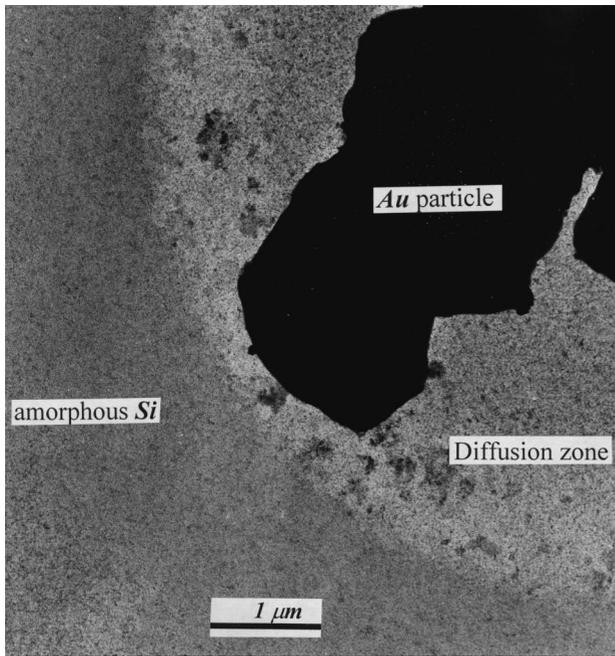


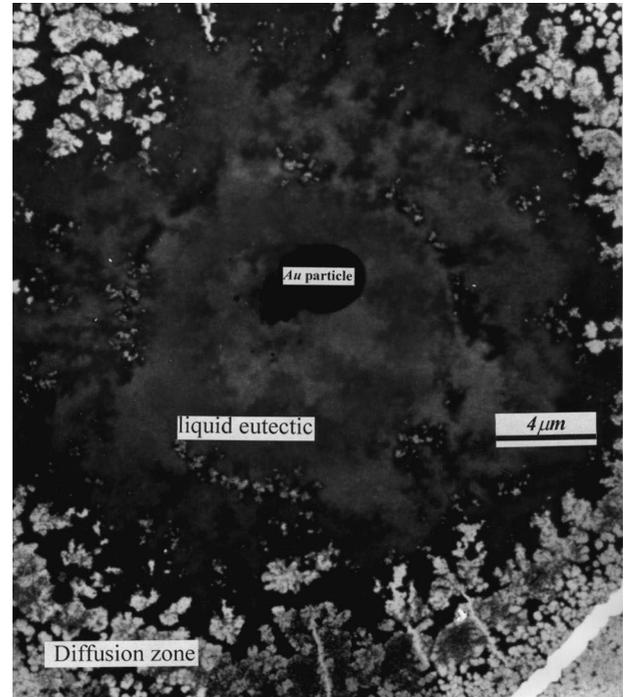
Fig. 3. Electron micrograph of the diffusion zone formed during isothermal annealing ($T=300^{\circ}\text{C}$) of gold particle on the surface of amorphous silicon film. The formation of a uniform product layer and propagation of the reaction front into the silicon amorphous film is observed.

tic alloy formed during isothermal heating, as a rule, does not lead to the formation of metastable crystalline gold silicide phases. Diffraction patterns of the decomposed alloy are a set of reflections of polycrystalline silicon and gold phases.

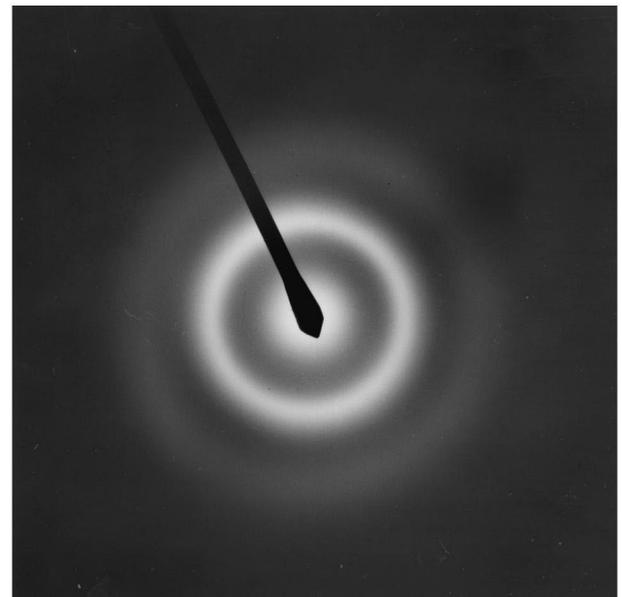
3.2. Changes of morphological and structural characteristics during the annealing of crystal (100) silicon film with gold particle

It was discovered during in situ investigation of the changes in morphological and structural characteristics resulting from the annealing of the crystal silicon (100) film with gold particle deposited onto its surface that the formation of eutectic alloy is substantially different from the above-considered sequence for the system amorphous Si/particle Au. Like in the studies of amorphous silicon interaction with gold particle, heating was performed either by high-intensity electron beam or using a special heater which caused substantial differences in the morphological characteristics of the process under investigation.

Heating with a high-intensity beam of accelerated electrons (10^{-1} A/cm^2) caused the formation of gold–silicon eutectic alloy which was accompanied by the propagation of the flat reaction front between the forming liquid eutectic alloy and single-crystal silicon. The reaction front formed during heating between liquid eutectic alloy and single-crystal silicon had a strict orientation relation-



(a)



(b)

Fig. 4. (a) Electron microphotograph of the diffusion and liquid eutectic zones formed during the interaction between gold particle and amorphous silicon film during isothermal heating ($T=380^{\circ}\text{C}$). An increase in annealing temperature of the system amorphous Si/particle Au above the eutectic melting point is characterized both by the propagation of the amorphous silicon crystallization zone, the formation of amorphous compound and by the formation of eutectic alloy near gold particle. (b) SAD pattern from liquid eutectic alloy formed during the interaction between gold particle and amorphous silicon film during isothermal heating ($T=380^{\circ}\text{C}$). Diffraction patterns of the liquid eutectic alloy is a set of diffuse rings with maximum of interplanar distances $d=2.45 \text{ \AA}$ and $d=1.15 \text{ \AA}$.

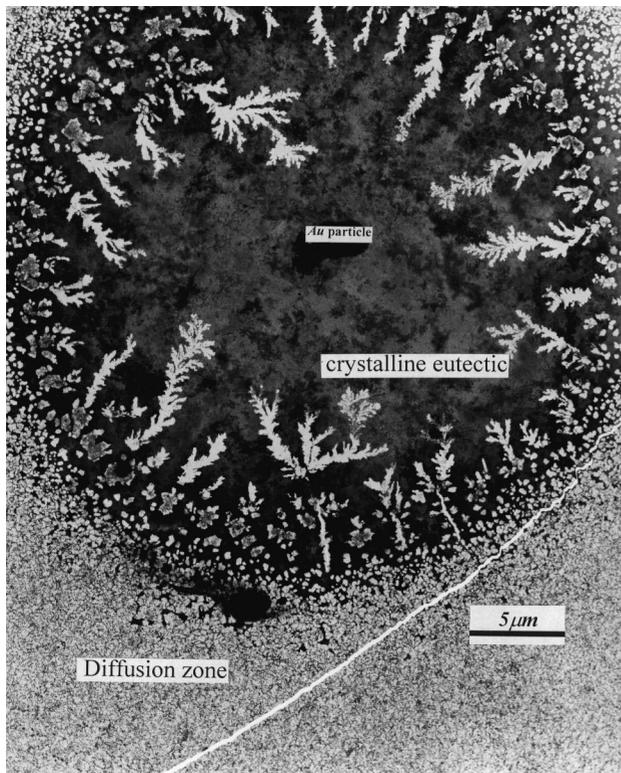


Fig. 5. Dendrite crystallization of the solid eutectic gold-silicon alloy obtained by the interaction between gold particle and amorphous silicon film at $T=380^{\circ}\text{C}$.

ship to the crystallographic axes of single crystal (100)Si. The direction of front movement was strictly coincident with the directions of the type [100]Si (Fig. 6).

Along with this, in the regions of single crystal silicon

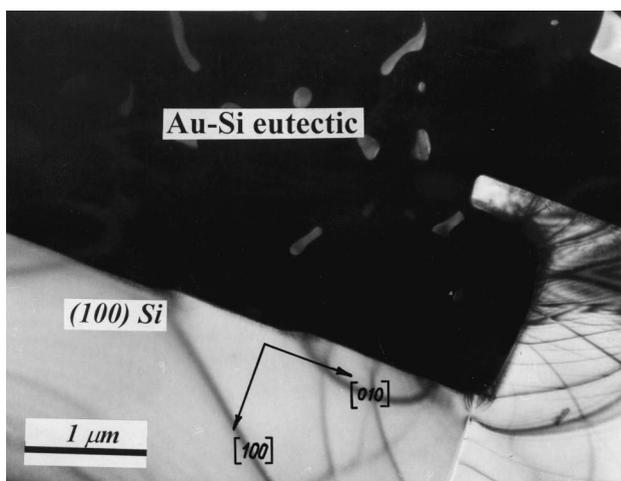
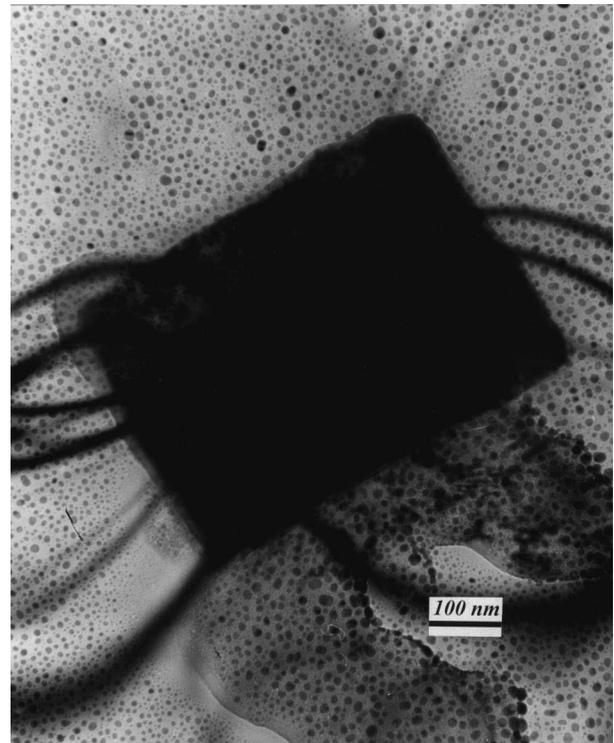
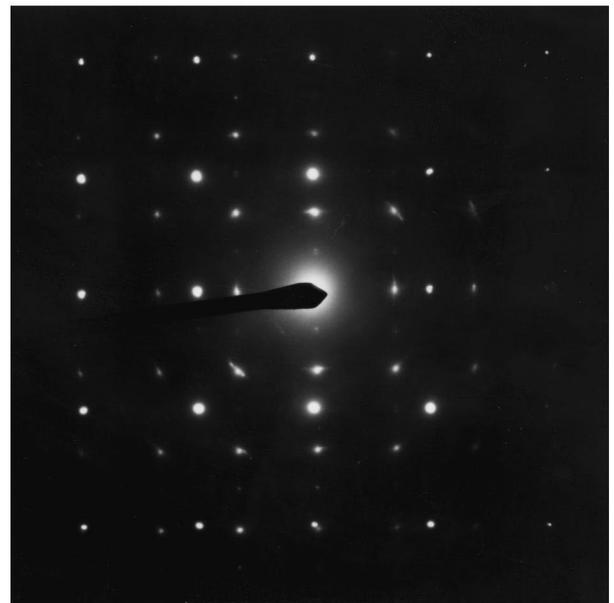


Fig. 6. Electron microphotograph of oriented formation of eutectic melt in the system gold particle-crystal (100) silicon ($T=380^{\circ}\text{C}$). The reaction front formed during heating between liquid eutectic alloy and single-crystal silicon had a strict orientation relationship to the crystallographic axes of single crystal (100)Si.

film located rather far from the eutectic phase (at a distance of several micrometers) we observed the deposition of square-shaped crystals and fine gold particles (Fig. 7a).



(a)



(b)

Fig. 7. (a) The formation of square crystals and fine gold particles at the cold regions of the sample under investigation during the formation of eutectic alloy gold-silicon under electron beam heating. (b) Electron diffraction from the square crystals of (a), exhibiting the presence of orientation correspondence to the silicon (100) crystal matrix.

Electron diffraction from the deposited crystals was substantially different by the structural characteristics from crystal silicon and gold. In some cases, the crystals thus discovered exhibited orientation correspondence to the single crystal silicon substrate (Fig. 7b). According to the data obtained, the formed phases correspond to the formation of metastable gold silicide.

In situ investigation of this system in isothermal conditions showed that the formation of eutectic alloy from crystal silicon and gold is observed at a noticeable rate at temperatures much above the eutectics melting point. In some cases, in order to observe the formation of eutectics, the system was to be heated up to 500°C. However, after the first «drops» of liquid eutectics appeared, the process goes on at temperatures below this point and is ceased at a temperature below the eutectics melting point. Similarly to the case of heating by electron beam, the movement of liquid eutectics front takes place into single crystal silicon and is oriented with respect to the crystallographic axes of single crystal silicon. Cooling of the liquid eutectic alloy leads to the crystallization of the melt and to the evolution of dendrite crystals of silicon and crystals of gold in the crystal silicon matrix (Fig. 8). It is natural that crystallization and the decomposition of eutectic alloy should be accompanied by the decrease of crystal phase volume with respect to the liquid phase which is really observed in the in situ experiments. After cooling, the formation of transition zone between the crystal eutectic alloy and the initial silicon matrix (Fig. 9a) is observed. The transition zone is composed of the particles with a size of several to tens of nanometer. As a rule, the concentration of particles released in the transition zone increases when approaching the crystallized eutectic alloy. Electron diffraction patterns from fine particles evolved during crystallization are unambiguous evidence of the topotaxial formation of gold silicide phase (Fig. 9b) which is exhibited in the patterns by the presence of ordered reflections (superlattice) with

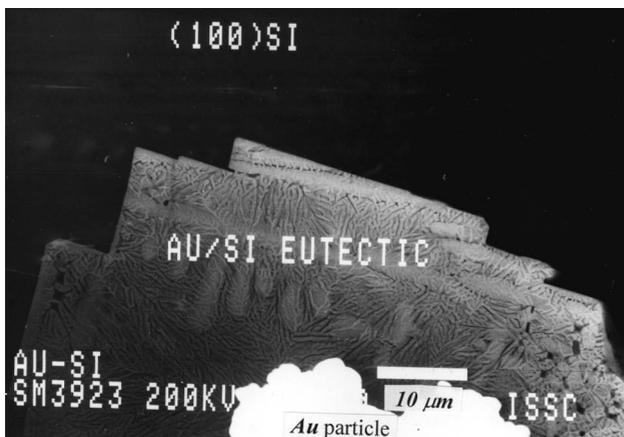
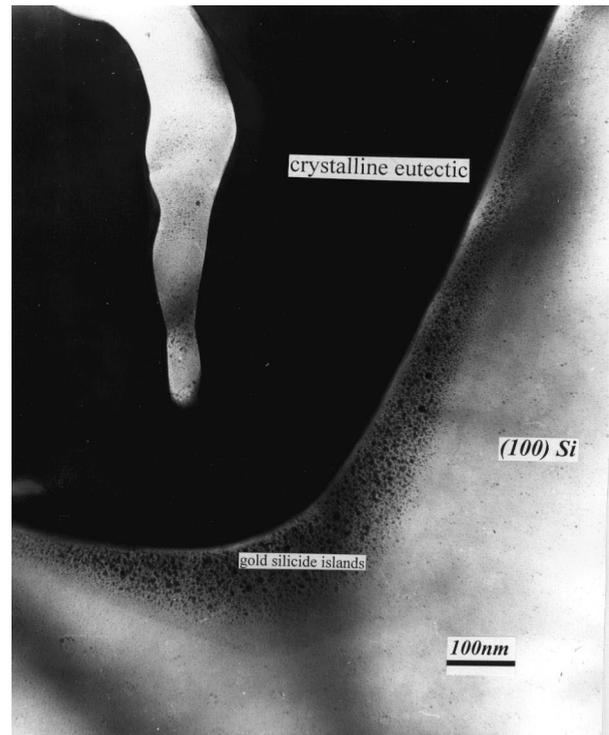
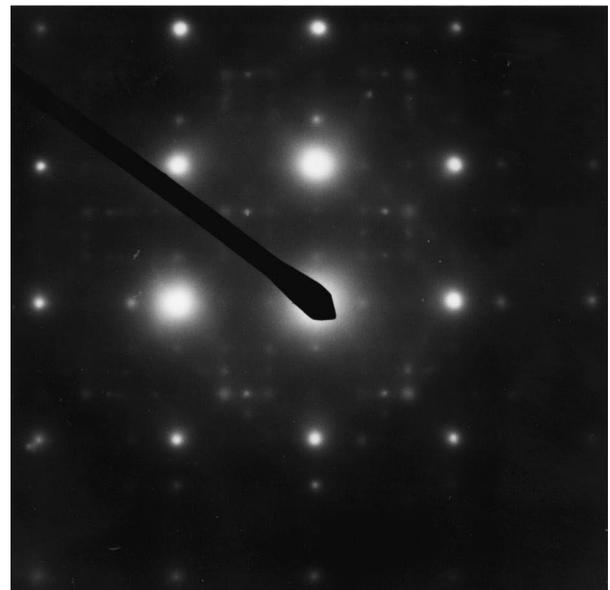


Fig. 8. SEM micrograph of the formation of dendrite silicon crystals and crystal gold on the (100) surface of crystal silicon matrix during the cooling of the liquid eutectic melt.



(a)



(b)

Fig. 9. (a) Electron microphotograph of the evolution of nano-sized particles at the interface between crystal eutectic and the single crystal silicon substrate after cooling to $T=20^{\circ}\text{C}$. (b) SAD pattern from nano-sized particles formed at the interface Au/Si eutectic-crystalline (100) Si after crystallization (a). SAD patterns from fine particles are evidence of the topotaxial formation of gold silicide phase which is exhibited in the patterns by the presence of ordered superlattice reflections.

much larger interplanar distances with respect to gold or silicon.

3.3. Investigation of the changes in morphological characteristics of the system single crystal gold film–silicon particle during annealing

In order to reliably consider diffusion processes that occur during the formation of eutectic alloy in the system silicon–gold, we performed in situ investigations of the changes of morphological and structural characteristics of the system during annealing when a gold single crystal film was used as a substrate. It was found that during the annealing of the (100)Au film–Si particle system at temperature below the melting point of eutectic alloy no substantial morphological and structural changes in single crystal gold film and silicon particle are observed within 10 min. Increase of annealing temperature above the eutectic melting point caused the formation of pores in the regions of single crystal gold film that were adjacent to silicon particle (Fig. 10). The formation of pores in single crystal film was observed even at a distance of several micrometers from the silicon particle. The pores were perfect rectangles oriented along the [100] and [010] crystallographic directions of the single gold crystal film. Pore size increased with increasing annealing time; the

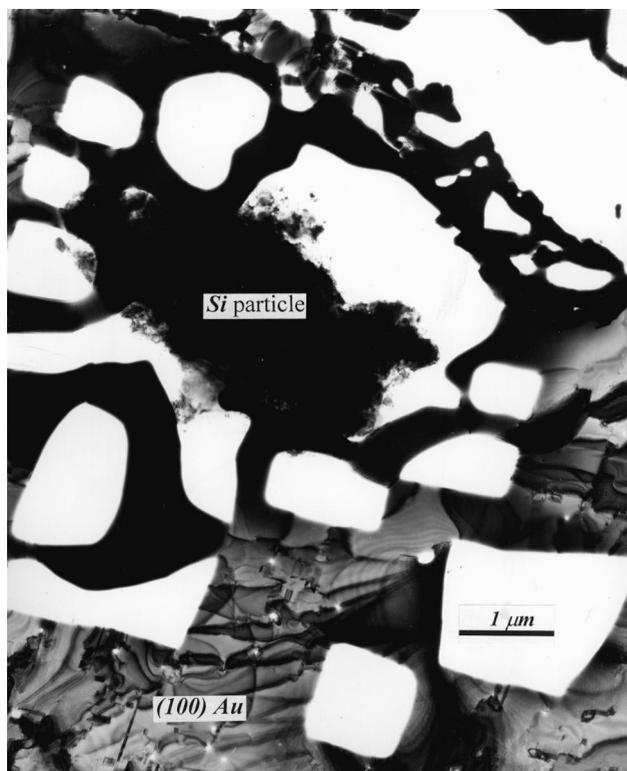


Fig. 10. Pore formation in single crystal (100) gold film in the regions adjacent to silicon particle during the annealing of the sample above the eutectic melting point.

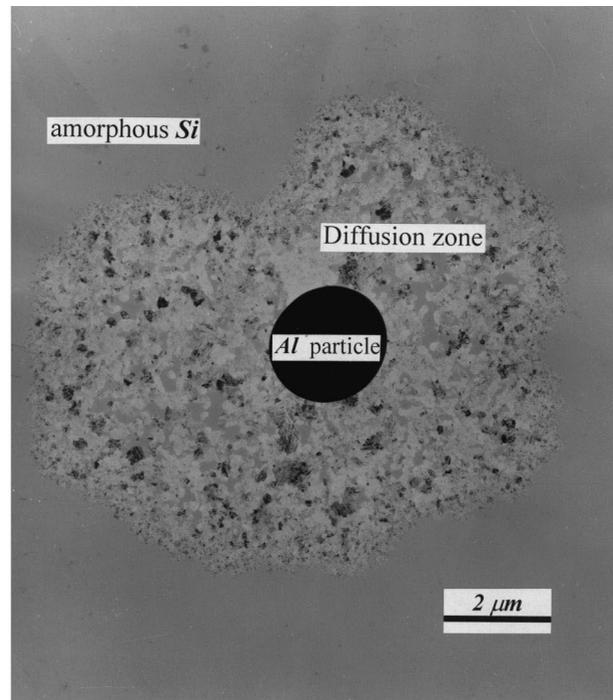
formation of «tentacles» was observed between the silicon particle and single crystal film.

3.4. Change in morphological and structural characteristics during the annealing of amorphous silicon film with aluminum particle

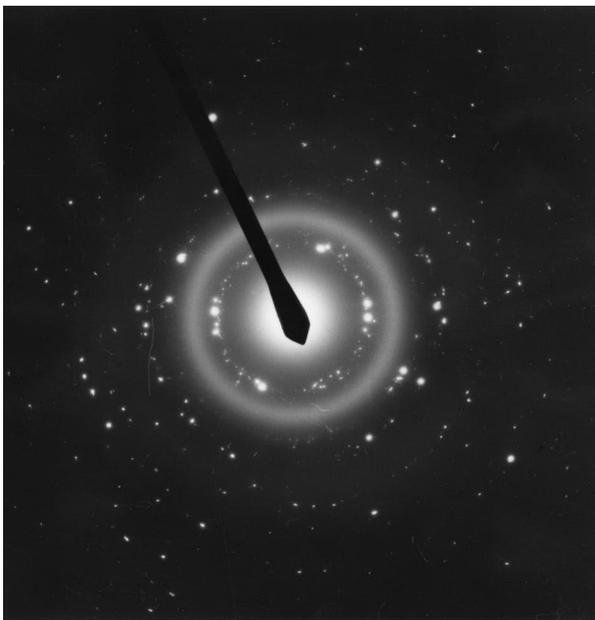
In order to reveal general features characteristic of the formation of eutectic alloys, along with the gold/silicon system, we studied aluminum/silicon system.

In situ investigations of the formation of eutectic alloy during annealing of the amorphous silicon film with aluminum particle on it showed that, independent of heating method (either in a special holder for heating the samples in electron microscope, or by electron beam), the interaction starts at 500°C that below the eutectics melting point. The formation of reaction front and its propagation into the amorphous silicon film is observed (Fig. 11a). The propagation of reaction front is accompanied by silicon crystallization and the formation of amorphous compound. This is confirmed in electron diffraction patterns by the presence of polycrystal silicon reflections and the diffuse halo with the maximum corresponding to the interplanar distance of $d=2.41 \text{ \AA}$ (Fig. 11b). This value is somewhat larger than the interplanar distance $d_{(111)}=2.33 \text{ \AA}$ for crystal aluminum which, in our opinion, is due to the formation of metastable amorphous aluminum silicide. In contrast to the above-considered system gold/silicon, cooling to room temperature leads to the disappearance of the reflections of the amorphous phase; only the reflections of silicon and aluminum crystal phases are observed in the electron diffraction patterns (Fig. 11c).

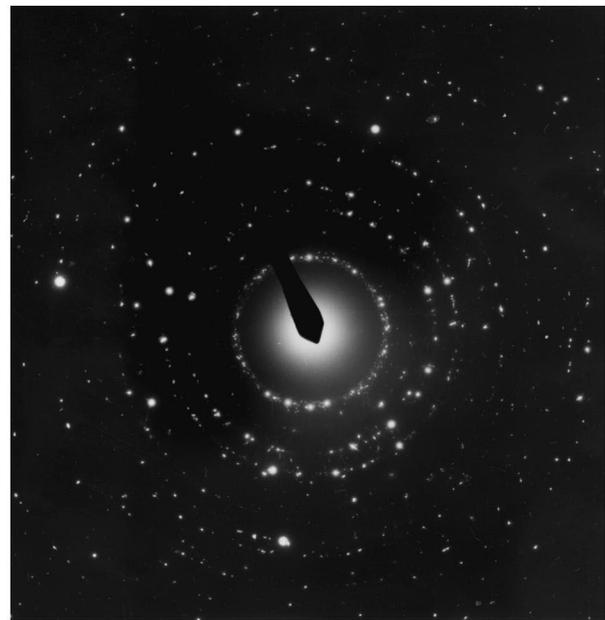
An increase in the annealing temperature up to 640°C in the system amorphous Si/particle Al above the eutectics melting point is characterized by the propagation of amorphous silicon crystallization zone and the formation of amorphous compound, as well as by the formation of the eutectic alloy in the vicinity of the aluminum particle (Fig. 12). The formation of eutectic alloy is accompanied by a substantial decrease of the size of aluminum particle and a simultaneous increase of the zone of eutectic liquid alloy. Decrease of annealing temperature below the eutectics melting point leads to the crystallization of the eutectic alloy. Unlike the dendrite crystallization of eutectics in the system Si/Au, the formation of crystal eutectic of Si/Al leads to the evolution of small silicon crystals inside the polycrystal aluminum matrix. It should also be noted that for the system Si/Al the crystallization of eutectic alloy in very rare cases had caused the formation of crystal metastable silicide phases of aluminum. The formation of these phases was observed only under rapid cooling of liquid eutectics produced by electron beam heating. In this case, electron diffraction patterns exhibited reflections of the crystal phase with the parameters substantially exceeding the interplanar distances characteristic of silicon and aluminum.



(a)



(b)



(c)

Fig. 11. (a) Electron microphotograph of the diffusion reaction zones in the system: aluminum particle-amorphous silicon which formed during heating at 500°C. The propagation of reaction front is accompanied by the crystallization of silicon and the formation of amorphous compound. (b) SAD pattern from the diffusion zone in the system: aluminum particle-amorphous silicon under annealing at $T = 640^\circ\text{C}$. The reflections of polycrystal silicon and amorphous compound are present in the patterns (c) SAD pattern from the diffusion zone in the system: aluminum particle-amorphous silicon cooled to room temperature. The reflections of polycrystal silicon and aluminum are present in the patterns.

3.5. Changes of morphological and structural characteristics during the annealing of crystal (100) silicon film with aluminum particle

When performing in situ studies of the changes in morphological and structural characteristics during the

heating of crystal (100) silicon film with aluminum particle deposited onto it, we discovered that the formation of eutectic alloy has some common features but has also some substantial differences from the system considered earlier: (100)Si foil/particle Au. The formation of eutectic alloy is observed between the solid components but at

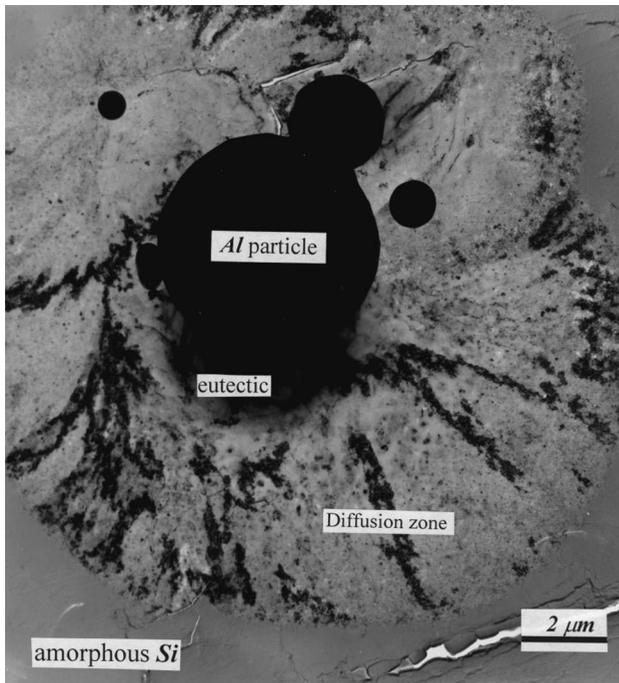


Fig. 12. Electron microphotograph of the diffusion zone and eutectic alloy formed during the interaction of the aluminum particle with amorphous silicon film under isothermal conditions ($T=640^{\circ}\text{C}$).

temperature somewhat higher than the eutectics melting point. The propagation rate of the front of liquid eutectics observed in this case is much lower than that observed during the formation of eutectics in the system gold–

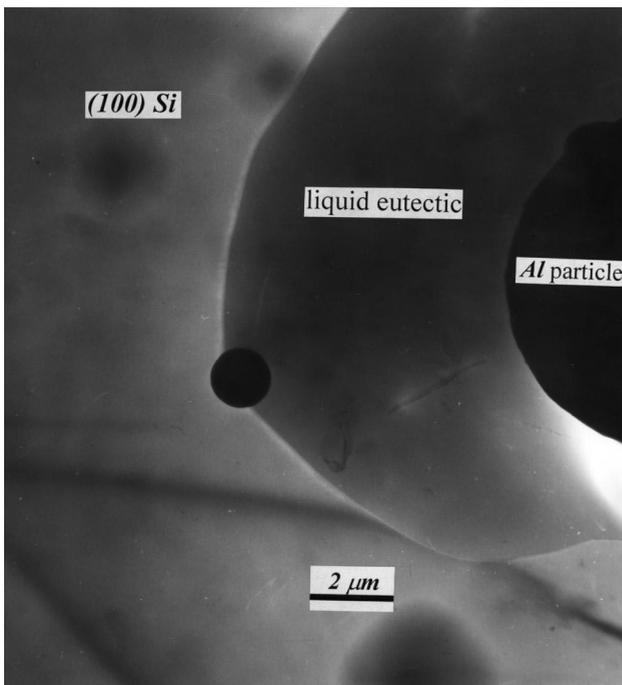


Fig. 13. Electron microphotograph of liquid eutectic alloy formed during isothermal annealing of the aluminum particle deposited on the surface of single crystal silicon.

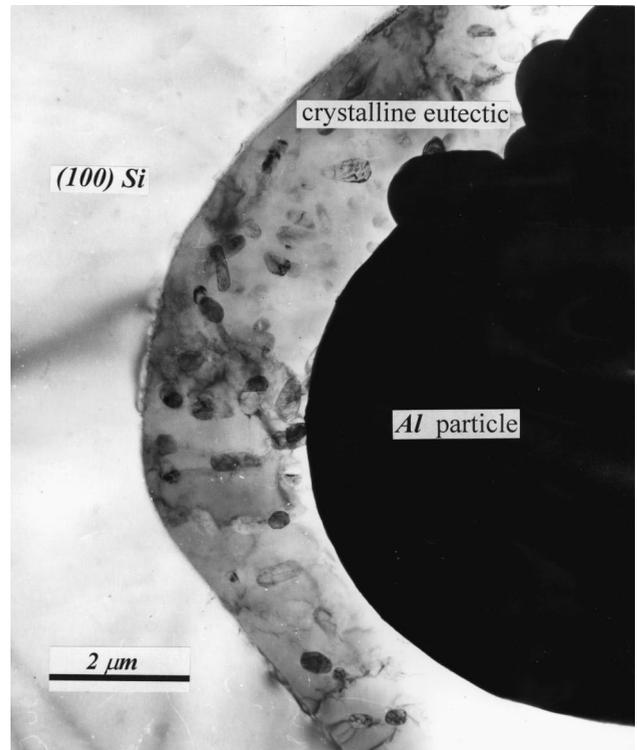


Fig. 14. The evolution of silicon crystals in the volume of aluminum matrix during the cooling of the eutectic alloy in the system: Si(100)–Al particle.

silicon. The movement of the reaction front between the formed liquid eutectic alloy and single crystal silicon does not follow any selected directions with respect to the crystallographic axes of single crystal silicon. The interface between liquid eutectics and crystal silicon is round (Fig. 13). Electron diffraction patterns of the interface between crystal silicon and liquid eutectics exhibit the reflections of single crystal silicon. Besides, an amorphous halo is present and its intensity maximum corresponding to the interplanar distance of $d=2.41 \text{ \AA}$. Cooling of the eutectic alloy leads to crystallization and to the evolution of silicon and aluminum phases (Fig. 14). This is accompanied by substantial shrinking of the eutectics (a decrease of the size of reaction zone is observed). Similarly to the annealing of aluminum particle on the surface of amorphous silicon, prolonged annealing of the system: crystalline (100)Si/particle Al leads to a decrease of aluminum particle size. At present one cannot succeed in discovering any species evolved at the interface between crystal eutectic alloy of aluminum and silicon, on one side, and the initial crystal silicon on the other.

4. Discussion

In situ investigation of eutectic alloy formation in the systems: amorphous Si/particle Au, crystalline (100)Si/particle Au, amorphous Si/particle Al and crystalline

(100)Si/particle Al allowed us to obtain some interesting and unusual experimental data that in some cases do not coincide with the literature data reported earlier.

When studying the changes of morphological and structural characteristics of the formation of eutectic alloys in the systems amorphous Si/particle Au, amorphous Si/particle Al, we observed the formation of the intermediate diffusion zone between the metal particle and amorphous silicon. The evolution of crystal silicon and the formation of amorphous compounds occur in this zone. Similar interplanar distances characteristic of the maximum intensity of the amorphous halo ($d=2.43$ Å for the system silicon/gold and $d=2.41$ Å for the system silicon/aluminum) as compared to the interplanar distances of crystal metals ($d=2.35$ Å for gold and $d=2.33$ Å for aluminum) allow us to conclude that amorphous silicides of gold and aluminum are formed. An additional confirmation of the formation of amorphous silicides can be the fact that the halo of the amorphous compound disappears when the system silicon/aluminum is cooled. After cooling only reflections of polycrystal silicon and aluminum are observed in electron diffraction patterns of the transition diffusion zone. This fact is the evidence that amorphous gold silicide formed during annealing is more stable than amorphous aluminum silicide.

The formation of metastable gold silicides is rather well-known process which takes place when gold film is deposited onto single crystal silicon planes [10–12], when the deposited gold film on the surface of silicon is annealed [13], when gold–silicon system irradiated with ions [14,15], when the melt is quenched [16], as well as during low-temperature solid-phase interaction of amorphous silicon with polycrystal gold in multilayer compositions [17,18]. However, in all the cases mentioned above, unlike the case of amorphous silicide formation discovered by us, as a rule, the formation of crystal metastable silicide phases was observed. These metastable Au–Si phases in many cases were decomposed under heating to form the equilibrium silicon and gold phases.

In our opinion, crystallization of amorphous silicon observed during the annealing with gold and aluminum is directly connected with the formation of amorphous metal silicides. Supersaturation of amorphous silicon during the diffusion of gold (or aluminum) under heating leads to the decomposition accompanied by the evolution of crystal silicon and amorphous metal silicide. Another evidence in favour of this mechanism of silicon crystallization during the annealing of the interacting pair silicon–metal is the experimental observation that under electron beam heating in the system amorphous Si/particle Au the transition diffusion zone is composed of periodic concentric layers of products with different intensities. Since diffraction characteristics obtained from different layers of this diffusion zone were the evidence of the identity of their composition differing only in the intensity of electron absorption, one can conclude that the concentration of amorphous gold silicide changes periodically. The ob-

served periodic change of the concentration of reaction products during the annealing of amorphous Si/particle Au coincides well known the morphological characteristics observed during the decomposition of supersaturated solid solutions [19]. As we have already mentioned, periodic evolution of reaction products is characteristic only for the heating with electron beam. Under electron beam heating, unlike under isothermal conditions, the system conditions can provide reaching large temperature gradients, high diffusion rates and consequently high supersaturation. It is most likely that the supersaturation of amorphous phase during isothermal annealing does not reach large values which provides uniform evolution of crystal silicon during the decomposition of metastable amorphous metal silicide.

Predominant diffusion of gold during the annealing is also confirmed by the experimental results on the changes of morphological characteristics in the system: single crystal (100) gold film–silicon particle. The heating of this system of interacting components was shown to lead to the formation of oriented pores in single crystal gold film in the regions adjacent to silicon particle. According to these data we can conclude that the formation of regular-shaped pores during the annealing of the systems under investigation is connected with metal diffusion along the ways of accelerated diffusion, and the sink of vacancies into grain boundaries and twin boundaries. This leads to the «dissolution» of some most defect-rich grains (due to accelerated metal diffusion from these grains and due to the sink of vacancies in them). The «dissolution» process leads to the oriented pore formation in single crystal gold films.

The movement of crystallization front into the amorphous silicon film (Fig. 1a) and the «dissolution» of single crystal gold film (Fig. 10) in our opinion, is an unambiguous evidence of the preferential diffusion of metal atoms in silicon. The experimental result obtained in the present study about predominant diffusion of gold atoms into silicon is in contradiction with the statements of the major part of previous works in which authors assumed that the formation of eutectic alloy is accompanied by the preferential diffusion of silicon into metal.

Another unusual experimental fact discovered in our present work is the oriented growth of liquid eutectic in the system crystalline (100)Si/particle Au. Unlike the oriented formation of liquid eutectics in the system crystalline (100)Si/particle Au, the formation of eutectics during the annealing of crystalline (100)Si/particle Al occurs isotropically.

It is well known that the oriented crystal growth in solid-phase transformations is rather widespread. It is called topotaxial transformation. In the case under consideration, we observe the oriented formation of liquid eutectic alloy in the interaction of solids: $\text{Au}_{\text{Solid}} + \text{Si}_{\text{Solid}} \rightarrow (\text{Au,Si})_{\text{Liquid}}$. A process analogous to this one exists, in our opinion, in the dissolution of etch pits. In spite of many theoretical considerations trying to explain experimental facts observed during the etching of crystals,

there is no universal theory that would be able to explain various aspects of 'simple' dissolution of crystals. Experimental results and theoretical ideas concerning the processes involved in liquid-phase etching of crystals are systematized most completely by Sangval [20]. According to this author, the rate of crystal dissolution and the morphology of etch pits depend on the nature of crystal, crystallographic orientation of the surface, presence of defects in the crystal, nature and composition of etchant, concentrations of components and admixtures in crystal and solvent, process temperature and many other factors. On our mind, the similar factors also can determine the shape of melt on the surface of solids during formation of liquid eutectic.

As we have already mentioned, along with the process of eutectics formation itself, the structure of the liquid eutectic alloy is of definite interest, too. In situ investigations showed that the diffraction patterns of liquid eutectic alloys are sets of diffuse rings characteristics of amorphous substances. Since interplanar distances characteristic of the maximum intensity of the diffuse reflections of liquid eutectic alloys are close to interplanar distances typical for crystal metals (gold or aluminum), we can assume that the short-range order characteristic of a metal (gold or aluminum) is conserved in liquid eutectic alloys.

In the present study we have demonstrated that the initiation of formation or crystallization of eutectic alloys by changing the intensity of accelerated electron beam leads not only to the formation of amorphous silicide in the diffusion zone. The cooling of eutectic melt is accompanied by the formation of stable crystal phases (silicon and metal), as well as metastable crystal metal silicide in the zone of eutectic alloy formation. This is most clearly seen in the systems amorphous silicon–gold. In our opinion, the formation of metastable crystal gold or aluminum silicides under this heating and cooling procedure is connected with the occurrence of quenching mechanism when tremendous temperature gradients can be achieved. Moreover, the formation of metastable compounds during the quenching of eutectic melt, on our mind, can prove that a metastable chemical compound is formed in liquid eutectic phase.

Crystallization of metastable gold silicide during heating by electron beam in the regions lying far from the zone of liquid eutectics (Fig. 7a) formation is also due to large temperature gradients. Since the heating by electron beam is local and it is practically impossible to maintain the temperature of the whole sample with high accuracy, this can lead to substantial overheating of the eutectic melt and to its evaporation. The deposition of evaporating melt occurs at "cool" parts of single crystal silicon which causes the stabilization and quenching of metastable crystal gold silicide.

In the present study we have discovered that topotaxial evolution of fine gold silicide islands at the boundary between crystal eutectic alloy and single crystal silicon is observed during the crystallisation of the eutectic alloy

Si–Au formed under isothermal conditions (Fig. 9a,b). Earlier the formation of gold silicide islands was observed by the authors [21,22] for the annealing of gold film deposited onto the (111) silicon face, and by the authors of [23] describing the formation of gold silicide islands during the deposition on (100) face of silicon single crystal. The authors of these papers believe that the formation of gold silicide is connected with chemical reactions at the interface. In our opinion, the observed topotaxial evolution of gold silicide islands at the interface between crystal eutectics and single crystal silicon (Fig. 9a), as well as the increase in the concentration of these islands with approaching the boundary of crystallised eutectic melt can be the evidence of diffusion-induced intrusion of gold atoms into crystal silicon structure before the formation of liquid eutectic alloy. The presence of this intermediate state (metastable gold silicide phase) corresponding in orientation to the crystal components of eutectic alloy can determine the process of eutectic melting in the system gold–single crystal silicon.

It is natural that we understand the possibility for the formation of eutectic alloys to be of more complicated character but the first in situ experiments on these processes allow us to arrive at a series of useful conclusions. Thus, in situ electron microscopic investigation of the formation of liquid eutectic alloys in the systems: amorphous Si/particle Au, crystalline (100)Si/particle Au, amorphous Si/particle Al and crystalline (100)Si/particle Al showed:

(i) For the systems: amorphous Si/particle Au and amorphous Si/particle Al, the formation of eutectics is preceded by the diffusion of metal into the amorphous silicon with the formation of metastable metal silicide.

(ii) Supersaturation and decomposition of the metastable amorphous metal silicide formed during the annealing of the systems amorphous Si/particle Au and amorphous Si/particle Al leads to the evolution of polycrystal silicon.

(iii) Morphological characteristics of the formation of liquid eutectics in the systems: crystalline (100)Si/particle Au and crystalline (100)Si/particle Al are similar to well-known morphological characteristics of the formation of etch pits in crystals. For the system: crystalline (100)Si/particle Au, oriented formation of liquid eutectic alloy is observed. The growth of eutectic melt during the annealing of the system crystalline (100)Si/particle Al occurs isotropically.

(iv) the crystallisation of liquid eutectic alloy leads to topotaxial evolution of gold silicide at the interface between crystal eutectics and single crystal silicon.

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