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Topological Analysis of the Effect of Annealing on the Grain-Boundary Structure of Polysilicon Films

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The effect of annealing on the grain-boundary structure of phosphorus-doped silicon films obtained by chemical vapor deposition was investigated by comparative analysis of atomic force microscopy data and existing model concepts. It is shown that the decisive factor for the applicability of the topographic model is the character of grain growth in the films. The model is applicable for annealing temperatures ≤ 1000 °C, at which normal grain growth is observed. In this temperature range, the distributions of different types of grain boundaries in polysilicon films are symmetric with respect to growing and disappearing boundaries. The structure of polysilicon films is equiaxed, there is no preferred orientation. At annealing temperatures > 1000 °C, anomalous grain growth takes place in the films, and the distribution of the types of grain boundaries indicates that the topological model is inapplicable in this temperature range. It can be assumed that the differences in the ratios of growing and disappearing grain boundaries in polysilicon films at different annealing temperatures are due to different mechanisms and driving forces of grain growth during normal and abnormal growth. With normal grain growth, the driving force prevails, that is caused by the difference in the density of dislocations in the adjacent grains. With abnormal grain growth, the driving force prevails, that is due to the difference in the average surface energy of the grains, which causes a sharp increase in the rate of grain growth.

Keywords: Polysilicon films, Grain boundaries, Grain growth mechanisms, Topological analysis.

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1. INTRODUCTION

One of the main elements of polycrystalline materials is grain boundaries. Grain boundaries are of great importance for controlling the properties of materials that is due to their significant impact on electrophysical, optical, mechanical and other properties, which are important from the point of view of practical applications [1-6]. Grain boundaries in polycrystals form a system of internal surfaces connected by means of a triple or multiple joints. Investigation of variations in angles at the joints of grain boundaries can provide information on the range of grain-boundary energy in a polycrystal, and, consequently, on the level of stability of the structure and stability of the material during various technological treatments [7, 8].

Despite the large number of studies of structure in materials, today there are many questions that relate to the structure and structural-energy characteristics of grain boundaries, as well as the kinetics of the processes that occur with their participation. The structural transformations of the grain-boundary structure under conditions of heat treatment and other technological influences are poorly studied.

The solution of such problems with real experiments is currently quite difficult because it requires research on the dynamics of the structure at the atomic level. Therefore, it is effective to use computer modeling methods that help to take into account and control the parameters of the processes that are being investigated with sufficient accuracy. Recently, in addition to experimental studies, much attention has been paid to the development of theories and the creation of models for the evolution of the grain-boundary structure of materials [9-12].

Comparison of model concepts with experimental data allows drawing conclusions about the mechanisms of grain-boundary transformations and predicting changes in the microstructure of materials and the nature of the distribution of grain boundaries under various influences. This helps to obtain materials with desired properties.

Only one work is known in this direction for silicon films [13]. In this work, a comparative analysis of the characteristics of the grain-boundary structure of nanosilicon films (film thickness 3-100 nm), experimentally observed by atomic force microscopy, with the existing model concepts is carried out. It was shown that the topological model of structural changes can be used to analyze the transformations of the grain-boundary structure only for undoped nanosilicon films with an equiaxed structure. For films with a fibrous structure, the topological model is unacceptable due to the presence in the films of a large number of multiple grain boundary junctions and grain boundary faceting. For silicon films of large thicknesses, such studies have not been carried out.

In this work, we investigated the effect of annealing on the grain-boundary structure of phosphorus-doped silicon films by comparative analysis of atomic force microscopy data and existing model concepts [11].

2. METHODS

Films of polycrystalline silicon were obtained by chemical vapor deposition in a reduced pressure reactor. The substrates were Si (100) wafers with a 100 nm SiO_2 layer. The deposition temperature was 630 °C, the film thickness was 500 nm. The films were doped with phosphorus by thermal diffusion (10^{21} cm^{-3}).

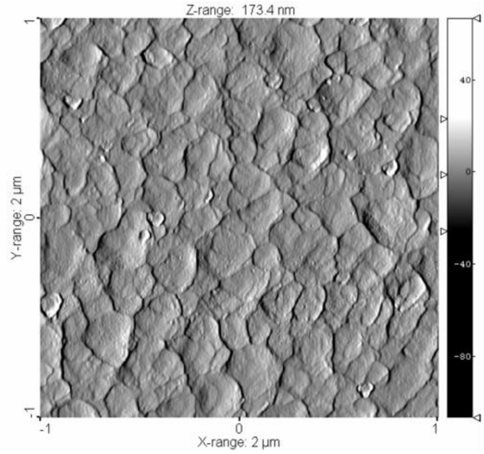
Annealing was carried out in an N_2 atmosphere in the temperature range 900-1150 °C for 30 min. As shown in [14], films obtained and annealed under such conditions have an equiaxed structure.

The grain-boundary structure of polysilicon films was analyzed using AFM images.

To study the structure of the films by transmission electron microscopy (TEM), the films were thinned in the plane of the substrate by chemical etching in a mixture of $HF{:}HNO_3$ (1:5).

3. RESULTS AND DISCUSSION

For topographic analysis of the grain-boundary structure of polysilicon films depending on the annealing temperature, we used the AFM images shown in Fig. 1. Several tens of grain boundaries of each type were analyzed. The topographic analysis was carried out within the framework of the model [11], which is based on the assumptions that low-energy boundaries have, on average, a larger area than high-energy ones, and the probability of disappearing for a high-energy boundary is greater than for a low-energy one. For the analysis within the framework of this model, we took into account such characteristics of the grain-boundary structure of polysilicon films as the configuration of the joints of grains and the value of the angles between the boundaries at the joints. Changes in these characteristics depending on the annealing temperature were analyzed.



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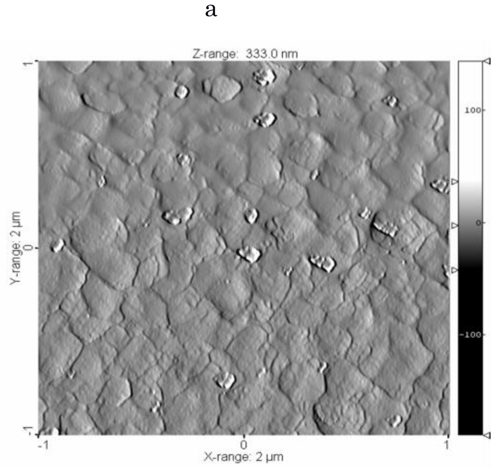

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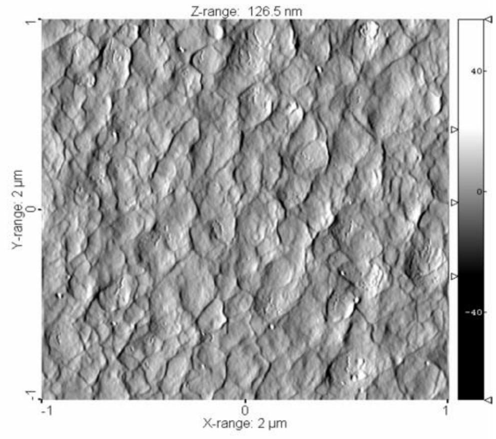
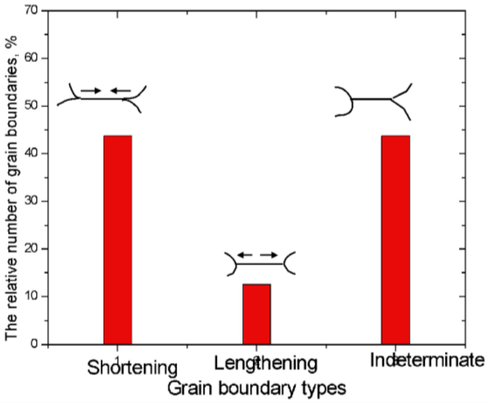


c

Fig. 1 – AFM images of the surface of polysilicon films without annealing (a) and annealed at temperatures of 900 °C (b) and 1150 °C (c)

In the model [11], only triple joints of grain boundaries are considered. It is believed that the curvature of the boundary in a two-dimensional image of the surface of the films is identified with the direction of movement. Each boundary between triple joints of grains is associated with four other boundaries (two in each triple joint) and different configurations are possible depending on the curvature of the boundaries that are in contact. The classification of grain boundary topologies, which is based on the curvature of boundaries, is given in [11]. It is believed that in the case when all four grain boundaries are concave, both triple joints will move towards each other and the length of the boundary between them will be reduced (shortening boundary). If all four boundaries are convex, both triple joints will move away from each other and the boundary between them will increase in length (lengthening boundary). Mixed configurations are possible when some of the grain boundaries are concave, and some are convex. All these grain boundaries can be classified as disappearing, growing, or indeterminate, respectively [11]. Fig. 2 illustrates the distributions of shortening, lengthening and indeterminate types of grain boundaries in polysilicon films annealed at various temperatures. It can be seen that for unannealed films and films that are annealed at a temperature of 900 °C, the ratios between different types of grain boundaries are similar. The relative number of growing boundaries is small for both cases, but for a temperature of 900 °C it is slightly higher. As is known [14, 15], at this annealing temperature, grain growth in films occurs by coalescence. With an increase in the annealing temperature up to 1150 °C, the relative number of lengthening and indeterminate grain boundaries significantly decreases, at the same time, the number of shortening grain boundaries increases significantly. At this annealing temperature, the mechanism of grain growth in films is the migration of grain boundaries [14, 15]. Comparative analysis of the data illustrated in Fig. 2 and the data on studies of yttrium aluminum garnet (YAG) presented in [11] shows that in the temperature range 630 °C (film deposition temperature) – 900 °C (annealing temperature), the distributions of different types of grain boundaries both for polysilicon films and YAG [11] are symmetrical with respect to shortening and lengthening boundaries. The structure of polysilicon films is equiaxed, there is no preferred orientation (i.e., grain orientation is random). With an increase in the annealing temperature up to 1150 °C, grains grow in polysilicon films and the situation with the grain-boundary structure becomes significantly different from that observed upon annealing in YAG. As shown in [11], upon YAG annealing, grain growth also occurs, as a result of which the grain-boundary structure changes in such a way that the symmetric distribution of grain boundaries transforms into an asymmetric one. In this case, the number of lengthening grain boundaries prevails in the annealed samples. This is in full agreement with model concepts, according to which grain growth is accompanied by a decrease in the number of high-energy grain boundaries and an increase in the number and length of low-energy grain boundaries. As can be seen from Fig. 2c, for polycrystalline silicon films, the distribution of types of grain boundaries at an annealing temperature of 1150 °C contradicts the model concepts.

It can be assumed that this difference is due to different grain growth nature in different temperature ranges. At annealing temperatures ≤ 1000 °C, normal grain growth takes place in polysilicon films, while at higher annealing temperatures anomalous grain growth is observed [15]. Fig. 3 shows electron microscopic images of the structure of polysilicon films in the plane of the substrate both before and after annealing at temperatures that correspond to normal and abnormal grain growth. The structure of polysilicon films is equiaxed, there is no preferred orientation.



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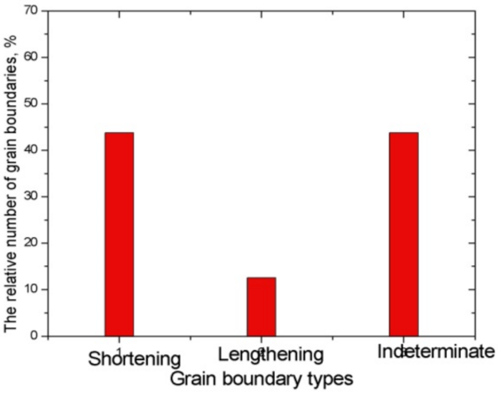

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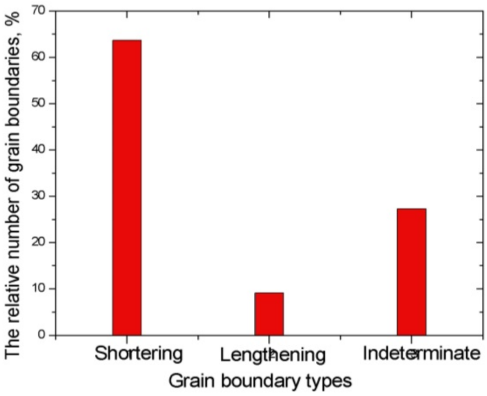
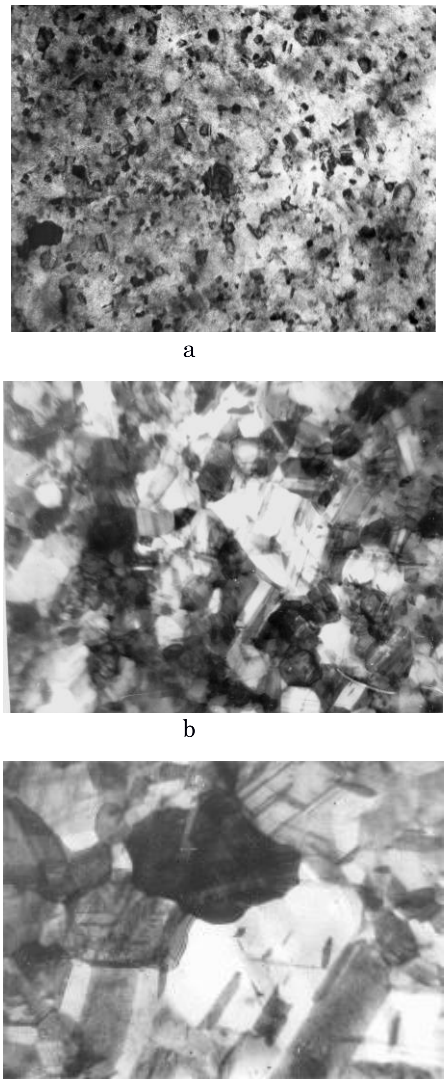


c

Fig. 2 – Distributions of shortening, lengthening and indeterminate types of grain boundaries in polysilicon films depending on the annealing temperature: a – unannealed films; b – 900 °C; c – 1150 °C ((a) shows schematic images of the types of grain boundaries and arrows indicate the directions of motion of the joints of grain boundaries)


a

b

c

Fig. 3 – TEM images of the structure of polysilicon films before annealing (a) and after annealing at temperatures of 900 °C (b) and 1150 °C (c), corresponding to the interval of normal (b) and anomalous (c) grain growth

As shown in [14, 15], grain growth in polysilicon films can be caused by the following driving forces: 1 – the driving force, which is associated with the difference in the density of dislocations in different grains; 2 – the driving force due to the differences in grain size; 3 – the driving force that is associated with the difference in average surface energy of the grains. The first two driving forces are predominant during normal grain growth. At the same time, the third driving force prevails in the case of anomalous grain growth during annealing at 1150 °C for a long time. Since the growth rate of anomalous grains is much higher than the growth rate of normal grains, it may happen that as soon as the film structure becomes columnar, the grain size exceeds the film thickness, the difference in average surface energy causes a sharp increase in the grain size and makes the topographic model inapplicable.

4. CONCLUSIONS

The study of the effect of annealing on the characteristics of the grain-boundary structure of phosphorus-doped polysilicon films with an equiaxed structure showed the following:

– the topological model of structural changes is applicable to the analysis of transformations of the grain-boundary structure of films in the temperature range ≤ 1000 °C, in which normal grain growth takes place;

– at higher annealing temperatures, anomalous grain growth is observed in the films, and the topological model is inapplicable.

– the reason for the inapplicability of the topographic model at an annealing temperature of 1150 °C is the predominance of the driving force for grain growth, which is due to the difference in the average values of the surface energy for different grains.

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Топографічний аналіз впливу відпалювання на зернограничну структуру полікремнієвих плівок

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Вплив відпалювання на зернограничну структуру легованих фосфором полікремнієвих плівок, що отримані методом хімічного осадження з газової фази, було проаналізовано шляхом проведення порівняльного аналізу даних атомної силової мікроскопії та існуючих модельних уявлень. Показано, що вирішальним фактором для застосування топографічної моделі є характер росту зерен в плівках. Модель застосовна для температур відпалювання ≤ 1000 °C, при яких спостерігається нормальний ріст зерен. Розподіли для різних типів границь зерен для полікремнієвих плівок є симетричними по відношенню до зростаючих та зникаючих границь. Структура полікремнієвих плівок рівноосьова, переважна орієнтація відсутня. При температурах відпалювання ≥ 1000 °C в плівках має місце аномальний ріст зерен, і розподіл типів границь зерен свідчить, що в даному температурному інтервалі топологічна модель є неприйнятною. Можна припустити, що відмінності у співвідношеннях зростаючих та зникаючих границь зерен в полікремнієвих плівках при різних температурах відпалювання обумовлені різними механізмами та рушійними силами росту зерен при нормальному та аномальному рості. При нормальному рості зерен переважною є рушійна сила, що обумовлена різницею густин дислокацій в суміжних зернах. При аномальному рості зерен переважає рушійна сила, яка обумовлена різницею середньої поверхневої енергії зерен, що призводить до різкого збільшення швидкості росту зерен.

Ключові слова: Полікремнієві плівки, Зерногранична структура, Механізми росту зерен, Топологічний аналіз.