ON THE NATURE OF LAYER SUBSTRUCTURE OF DOPED SILICON FILMS

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Abstract. In the paper the mechanism of the formation of the layer substructure of As-doped crystallites of poly-Si films, formed during pyrolysis of silane, is discussed. It is shown that the possibility of the layer substructure formation is controlled by the process of surface diffusion of As atoms over the surface of the growing Si grain.

1. INTRODUCTION

The films with composition modulations of the components with limited mutual solubility are of interest as promising functional materials of nanoelectronics. The possibility of production of compact nanocrystal heterostructures is shown in [1-4]. The investigation of regularities of structural formation in such systems is also important for a better understanding of the mechanism of self-organization processes during the growth of the films from the two-component vapour phase.

In the paper [5-6] it is shown for the metal systems Ag-Cu and Ag-Ni that in the narrow temperature range the nanocrystal structures with composition modulations are formed, which are the highly-dispersive layer compositions of the alternating thin mutually oriented plates of both phases up to 10-30 nm in diameter and with a thickness up to several nanometers, the formation of which is controlled by the process of diffusion layering from two-component flux. The aim of the present work is to investigate the layer substructure of As-doped polycrystal silicon films.

2. EXPERIMENTAL RESULTS

Si films were growth by pyrolysis of silane (SiH_4) on different substrates (SiO_2, Si_3N_4, (001) Si, (111) Si) with the presence of the doping component (AsH_3) in the gas phase in the range of the deposition temperatures T_s=800-1050 °C. The deposition was made in the set-up for epitaxial deposition with reactor of vertical type and the induction heating. In all the experiments the concentration of the impurity (AsH_3) was kept constant with respect to the main reagent (SiH_4). The concentration of SiH_4 in the gas phase was 0.2-3.4% by volume and that of AsH_3 was 0.005-0.085 % by volume. Using the electron microscopes UEMV-100K and EMV 100-M the investigation of the film substructure was made. The morphology of the film surface at different stages of growth was investigated by the replica method. The micrographs and electron diffraction patterns characterizing orientation, morphology of the film surface and grain substructure are presented in Figs.1,2.
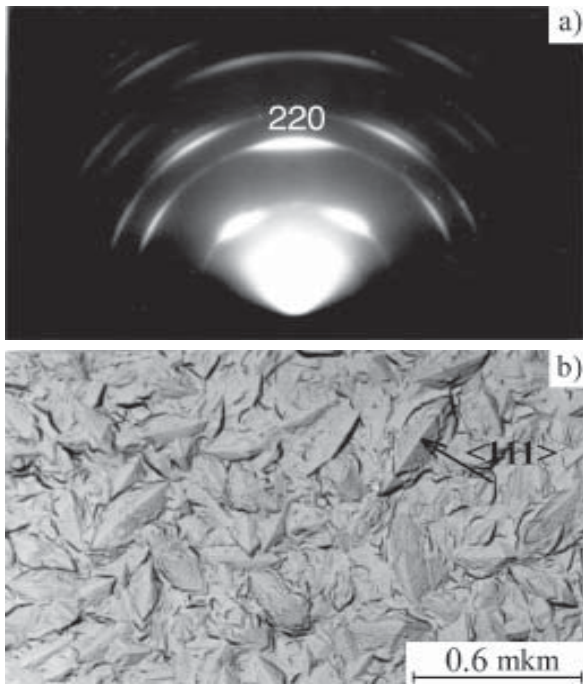
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Fig. 1. Orientation (a) and surface morphology (b) of Si-As film on SiO$_2$ substrate for T_s=850 °C.
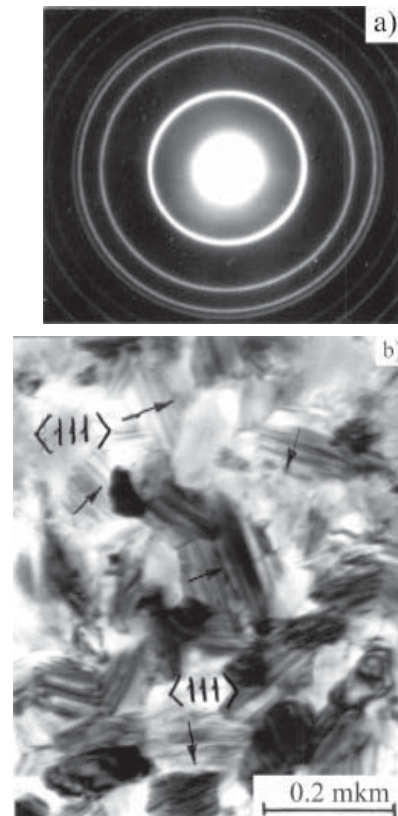

Fig. 2. Substructure of Si-As film on SiO$_2$ substrate for T_s=850 °C.

As shown in Figs. 1a and 1b, the films are characterized by the well-developed one-axis <110> texture and the relief of two levels, namely, the one connected with the nature of the crystallite intergrowth (without coalescence) and the other connected with the microsteps. The microsteps present the layer substructure of the grains, which is supported by the electron transmission of the films. This peculiarity is preserved for the whole range of T_s.

The broadening of 111 ring in the electron diffraction pattern (Fig. 2a) is also connected with the layer grain substructure. This broadening suggests that the silicon layers, which are thin ones in <111> direction, run along {111} planes normal to the substrate. The layer width was increasing with the deposition temperature increase from 5 nm (800 °C) to 80 nm (1050 °C). Fig. 3 illustrates this dependence of the layer width on temperature.

The experimentally determined dependence of the silicon layer width on temperature (Fig. 3) is of exponential nature, i.e.

$$L(T) = L_0 e^{-\frac{E}{kT}}. \tag{1}$$

The determined activation energy of the process E is about 1.8 eV. Thus, along with the diffusion accumulation of impurity on the growth front the width of Si layers may be also controlled by the other processes, in particular, surface diffusion of silicon atoms.

3. MODEL OF DIFFUSION LAYERING

To describe the formation kinetics of the layer substructure of Si grains, let's use the model of diffusion layering in two-component metal films with limited mutual solubility, developed by the authors in [7,8], with the difference in the methods of film formation in view.
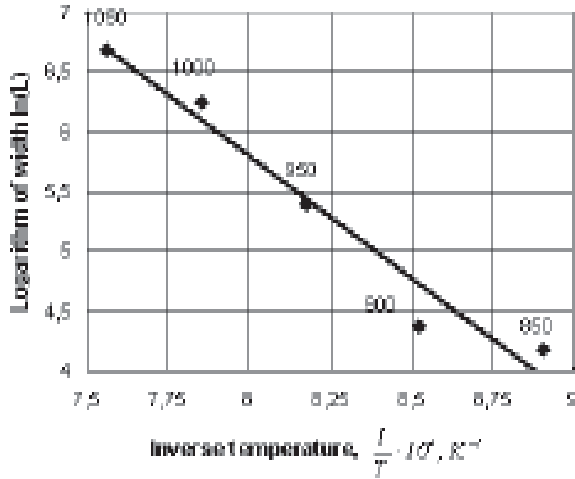
Fig. 3. Experimental dependence of the Si layer width on the substrate temperature.
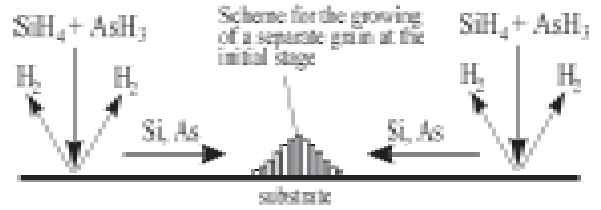

Fig. 4. The scheme for the layer formation at the initial stage of the film growth.

Fig. 4 shows the scheme for the growing of a separate grain at the initial stage with the fact in view that the decomposition reaction takes place on the substrate surface.

The free atoms of Si and As formed during the pyrolysis migrate over the substrate surface. The density fluctuations of the adsorbed atoms lead to the formation of the nuclei of a new phase.

In the present work the kinetics of the formation of two-component clusters was not investigated, but due to a great difference in the fluxes of the main and the doping components, arriving at the substrate, it is evident that the forming separate crystal grains should consist largely of silicon atoms. Since at the initial stages of deposition the separate silicon grains grow at the expense of lateral arrival of atoms over the substrate surface, the impurity (As) accumulates gradually on the grain side which is a close-packed plane (111). At some moment the As atoms suppress the growth of the crystalline matrix plate and a new plane Si (111) nucleates (possibly, in the twin orientation).

Following the intergrowth of the grains and the formation of a continuous film the subsequent formation of the layer substructure takes place at the expense of diffusion of impurity atoms over the surface of each grain. During the pyrolysis the As atoms, arriving at the surface of the formed Si layers, diffuse to the As interlayers. The silicon atoms build in their crystal lattice. Thus, the growth of Si and As layers in the vertical directions continues. Let's determine the values for the surface diffusion parameters for which this mechanism of diffusion layering will be realized.

The diffusion equation is written for the strip of L width (lateral size of silicon layer). The As interlayers are treated as infinite drains for the diffusing atoms

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} + R, \tag{2}$$

where $c(x,t)$ is the As concentration on the surface of the silicon layer; D the surface diffusion coefficient of As on silicon; R the number of arsenic atoms forming on the layer surface unit per unit time as a result of pyrolysis. The initial and boundary conditions are as follows

$$c(x,0) = 0,$$
$$c(0,t) = c(L,t) = 0. \tag{3}$$

The solution is written in the form

$$c(x,t) = \frac{2R}{L}\int_0^L\int_0^L\sum_{n+1}^{\infty}\exp\left(-\frac{n^2\pi^2 D(t-\tau)}{L^2}\right)\sin\left(\frac{n\pi\xi}{L}\right)\sin\left(\frac{n\pi x}{L}\right)d\xi d\tau, \tag{4}$$
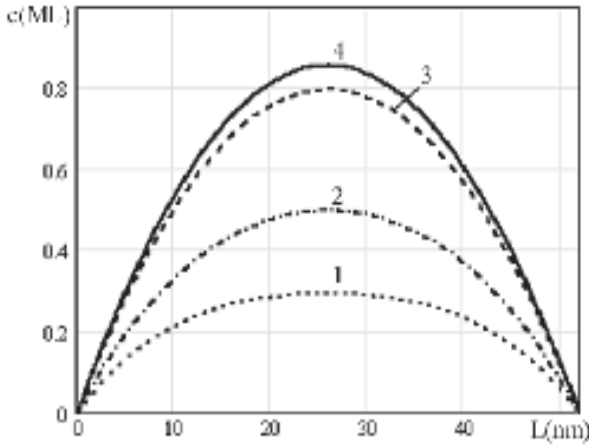
Fig. 5. Concentration profile of As (in monolayers – ML) for different times. T_s=1000 °C, L=52 nm, E_d=2.1 eV, 1 – t=0.05 s; 2 – t=0.1 s; 3 – t=0.3 s; 4 – t=1 s.
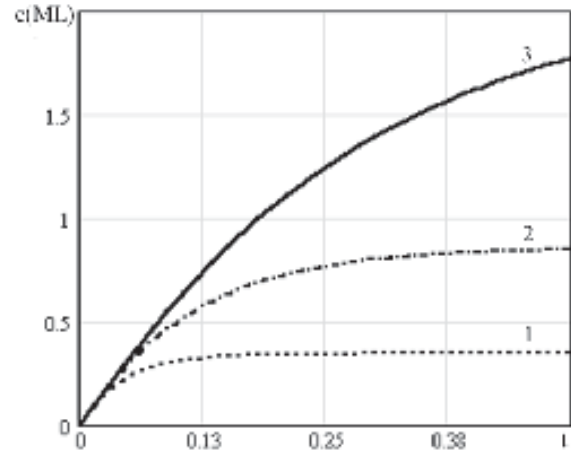
Fig. 6. Plots for dependence of As concentration in the middle of Si layer on time. T_s=1000 °C, L=52 nm, 1 – E_d=2.0 eV; 2 – E_d=2.1 eV; 3 – E_d=2.2 eV.

where L is the Si layer width.

The choice of values for R, L and D for the qualitative analysis of the results and conclusions of the theoretical model is of no basic importance. However, in view of the possibility of comparison with the results of the particular experiment, the following values were used in the calculations:

– R value was determined in accordance with the experimental parameters of the growth conditions in view of the arsine concentrations (AsH$_3$) in the gas phase not exceeding 2.5 % in all the cases, R=2.5·10^{19} m^{-2}·s^{-1};

– the value of activation energy of the surface diffusion of As atoms varied from 2 eV;

– the value D_0=5·10^{-3} cm^2·s^{-1} was determined from expression for the surface diffusion coefficient

$$D = D_0 e^{-\frac{Ed}{kT}} = \frac{1}{4}a^2 \nu \eta e^{-\frac{Ed}{kT}}, \tag{5}$$

where a is the lattice constant, ν the frequency of thermal vibrations ($10^{12}-10^{13}$ s^{-1}), η the possibility of the fact that the new adsorption site for the diffusing atom is vacant (in case of the surface diffusion one may assume η=1).

4. RESULTS AND DISCUSSION

The results of numerical calculations of impurity concentration profile for the silicon layer width and the evolution of this profile in time (Fig. 5) show that the stationary condition is achieved in a sufficiently short time, after which the flux of the arriving atoms of As is compensated by the diffusion to the layer boundary.

Fig. 6 shows the dependence of As concentration in the middle of the silicon layer surface on time. For the given temperature and the rate of atom arrival this concentration is determined by the values of activation energy of As diffusion on silicon and the layer width. Using the experimentally determined values of L, we may calculate the critical values of E_d at which the impurity accumulation on the surface of the growing Si layer does not exceed, in average, one monolayer of As, i.e. the following equation is fulfilled

$$c_{av} = \frac{1}{L}\int_0^L c(x,\infty)dx = 1 \ (ML), \tag{6}$$

where c_{av} is the average impurity concentration (in monolayers – ML), $c(x,\infty)$ – the concentration in the layer width in the stationary condition.

The calculations of critical values of E_d for the experimentally determined values of L give the minimal value 2.15 eV for T_s=1050 °C, and the maximal value 2.6 eV for T_s=800 °C. Since the mechanism of diffusion layering is realized for the whole range of temperatures used in the experiment, it may be stated that the real value of E_d should not exceed 2.15 eV. According to [9], the activation energy of the bulk diffusion of As in Si is in the range of 3.5-4.2 eV. Assuming the value of activation energy of the surface diffusion to be equal to the half of the activation energy of the bulk diffusion we may speak of its agreement with the range of permissible values of E_d.

5. CONCLUSIONS

During the growth of polycrystal As-doped silicon films the layer grain substructure is formed, the nature of which is connected with the impurity segregation on the front of the grain growth which leads to suppressing of the growth and subsequent nucleation of a new layer. The estimation of the value of activation energy of impurity surface diffusion for realization of the layer grain substructure has been made.

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