

A Model of the Evolution of the Au/Si Droplet Ensembles during Rapid Thermal Annealing at High Temperatures

A. Sarikov^a, A. Klimovskaya^b, O. Oberemok^c, O. Lytvyn^d
and O. Stadnik^{1, e}

V. Lashkarev Institute of Semiconductor Physics NAS Ukraine, 45 Nauki avenue, Kiev 03028, Ukraine

^aandrey.sarikov@gmx.de, ^bkaignn@rambler.ru, ^coberemok@isp.kiev.ua, ^dlytvyn@isp.kiev.ua, ^estadnik@isp.kiev.ua,

Key words: Si wire-like crystals, catalytic Au/Si droplet arrays, coarsening, coalescence, Smoluchowski equation, computer simulation.

Abstract. Formation of the patterns of catalytically active metal containing droplets on substrates is an important process for the growing Si wire-like crystals because it predetermines the main crystal parameters. Understanding physical mechanisms of droplet evolution during thermal treatments and derivation of associated parameters are the clue to the controlled formation of droplet ensembles and thus to the predicted growing Si wire-like crystals. In this work, the kinetics of the evolution of droplet ensembles on the surface of substrate as a result of coalescence and atom evaporation is studied theoretically. Obtained theoretical results are compared to the experimental data on the evolution of the ensembles of Au/Si droplets on Si substrate formed by rapid thermal anneals of thin gold film in the temperature range from 900 to 1050°C. The activation energy of droplet diffusion on the surface of substrates is estimated.

Introduction

The vapour-liquid-solid (VLS) process technology is one of the key technologies for the fabrication of Si wire-like crystals. Its important step is the formation of the arrays of catalytic metal containing droplets on the substrate that determine the positions and the sizes of grown wire-like crystals. Different techniques can be used to form the metal containing particles, such as, annealing of deposited thin films of metals until they break into separate islands, or the immobilization of metal colloids. Furthermore, electron beam or nanoimprint lithography [1], microcontact printing [2], and nanosphere lithography [3] can be used to structure the metal nanoislands for subsequent VLS growth of wire-like crystals.

The formed arrays of metal containing droplets are as a rule subjected to subsequent thermal anneals. During these anneals, self-organisation evolution of droplets (so called coarsening) takes place resulting in the modification of their distribution functions. The rate of droplet coarsening is determined by the fundamental rates involved in the coarsening mechanisms, which are usually the Ostwald ripening [4-6], the droplet coalescence [7-11], or the combination of both.

Multiple experimental observations support the coarsening of various droplet or island ensembles on the substrate surfaces by coalescence. First of all, such observations refer to the metal islands on metal substrates. The diffusion of Cu islands on Cu(100) substrates [12] and Ag islands on Ag(100) substrates [12, 13] have been observed by time resolved STM measurements. The islands reached up to several nm in size demonstrating that large islands are also able to move. The diffusion of large islands has been also observed for the As (islands up to 10 nm in diameter) on the graphite substrates [14] and 3D Au clusters on halide substrates already at room temperature [15-17]. In addition, the diffusion and coalescence of Au droplets on the surface of (111) Si substrates during the deposition of Au films by room temperature sputtering is demonstrated in [18].

This work is aimed at the simulation of the kinetics of the evolution of the arrays of catalytically active droplets as a result of coalescence taking into account also the evaporation of droplet constituent atoms from their surfaces. The effect of the time and the temperature of annealing as well as the evaporation rate of droplet constituent atoms on the droplet density and distribution function is studied. The comparison of the results of simulations with the experimental data has enabled to estimate the activation energy for the diffusion of Au/Si droplets on the Si substrates during the rapid thermal annealing at high (beyond 900°C) temperatures.

Experimental background

The catalytically active Au containing droplets on the surface of Si substrates were formed by a deposition of 3 or 5 nm thick gold films followed by rapid thermal anneals (RTA) during 20 s. Anneals at temperatures beyond 650°C initiated the film disjoining and the formation of the arrays of separate droplets whose patterns (droplet size and quantity) depended on the annealing

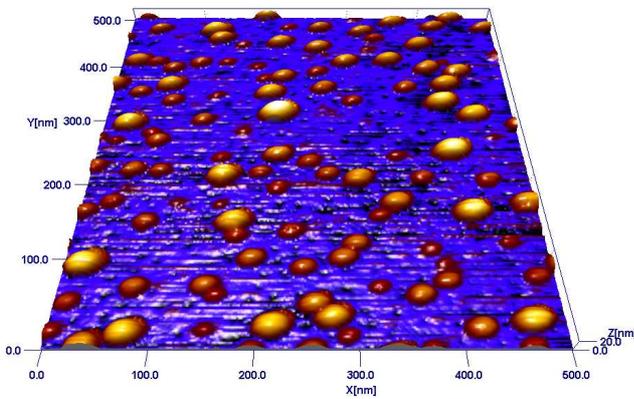


Fig. 1. AFM image of the Au/Si droplets on Si substrate formed by 20 s RTA treatment of 3 nm Au film at 1000°C.

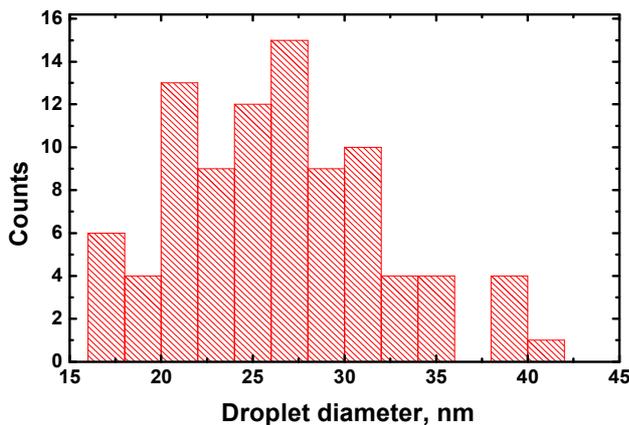


Fig. 2. Distribution functions of Au/Si droplets obtained after 20 s RTA of 3 nm Au film at 1000°C.

2 shows the histogram of the distribution of droplet diameters corresponding to the data in Fig. 1, which clearly reveals the non symmetrical logarithmic-normal like character of droplet distribution.

Theoretical model

Model of droplet coalescence. In the model of coalescence, the droplets migrating on the flat surface of the substrate and occasionally touching each other are considered. As a result, new droplets with the volumes equal to the sums of the volumes of coalesced droplets are formed. This process is considered to be limited by the diffusion of droplets on the surface of substrate. The evolution of the distribution function of droplets on size is described by the Smoluchowski equation in the following form [25]:

conditions. The prepared arrays were studied by atomic force microscopy (AFM). Fig. 1 shows an exemplary AFM image of the droplet array obtained after the RTA treatment of 3 nm gold film at 1000°C. An accompanying phenomenon to the breakdown of gold film is the dissolution of Si from the Si substrate. This process is characterised by the high reaction rate and the fast Si diffusion across the interface and within the Au. In result, the intermixing of gold with silicon atoms accompanied by the formation of a silicide-like solid solution at the interface occurs, as revealed experimentally and supported by molecular dynamic simulations (see Refs. (19), (20), and references therein).

High diffusion rates of Si in gold film coatings on silicon crystals have been reported by various groups [21, 22] that may mean the disjoining of the gold film containing already the concentration of Si corresponding to its saturation level.

Upon the formation of initial pattern, the droplets continue to evolve on the substrate due to the coarsening. During this process, the average droplet size increases and their density decreases. The characteristic feature of the distribution of droplets formed on the substrate surface, as a result of temperature stimulated disjoining of solid Au film, is the change of the character of this function from the symmetrical Gaussian-like to the strongly unsymmetrical logarithmic-normal like, which is pertinent to droplet coalescence [23, 24]. Fig.

$$\frac{\partial F_i}{\partial t} = \frac{1}{2} \sum_{j=1}^{i-1} k_{i-j,j} F_{i-j} F_j - \sum_{j=1}^n k_{i,j} F_i F_j \quad (1)$$

where $k_{i,j}$ are the kinetic coefficients of the interaction of droplets with the numbers of atoms i and j and F_m is the density of droplets containing m atoms, respectively. The first term in Eq. (1) describes the increase of the density of the droplets of size i due to the coalescence of the droplets of sizes $i-j$ and j , respectively. The second term describes the decrease of droplet density due to the coalescence with all size droplets.

The kinetic coefficients $k_{i,j}$ are determined by the diffusivities of droplets that in turn depend on the number of atoms in the islands [12]:

$$k_{i,j} \sim D_i + D_j = D_0 (i^{-\alpha} + j^{-\alpha}). \quad (2)$$

Here, D_i and D_j are the diffusivities of droplets having the numbers of atoms i and j , respectively, and D_0 is the temperature dependent diffusion constant.

We assume the random motion of droplets on the substrate surface with the diffusivity depending on their size. The kinetic coefficients of droplet interaction can be obtained from the precipitation theory in the following form:

$$k_{i,j} = 2\pi(D_i + D_j) \quad (3)$$

Using scaling of the diffusivity, $D_i = D_0 i^{-\alpha}$, the kinetic coefficients for the simplest case of $\alpha = 1$ become as follows:

$$k_{i,j} = 2\pi D_0 \left(\frac{1}{i} + \frac{1}{j} \right) \quad (4)$$

Such a mechanism of droplet diffusion corresponds to the correlated evaporation/condensation mechanism or to the terrace diffusion mechanism that have the same scaling behaviour of diffusion coefficient [18].

Another option is the periphery diffusion mechanism that corresponds to $\alpha = 2$. The kinetic coefficients in this case are expressed as follows:

$$k_{i,j} = 2\pi D_0 \left(\frac{1}{i^2} + \frac{1}{j^2} \right) \quad (5)$$

It is convenient to formulate the problem of the evolution of droplets on the surface of substrate due to their coalescence in terms of normalised droplet densities, v_i , and time, τ , that are expressed as follows:

$$v_i = \frac{F_i}{F_{tot}} \quad (6)$$

$$\tau = 2\pi D_0 F_{tot} t \quad (7)$$

where F_{tot} is the total initial density of droplets on the substrate surface. In the normalised formulation of the problem, the increase in the treatment temperature is taken into account by the respective contraction of the time scale. Eq. (1) in normalised parameters takes the following form:

$$\frac{\partial v_i}{\partial \tau} = \frac{1}{2} \sum_{j=1}^{i-1} \chi_{i-j,j} v_{i-j} v_j - \sum_{j=1}^n \chi_{i,j} v_i v_j \quad (8)$$

where new kinetic coefficients $\chi_{i,j}$ depend only on the sizes of coalesced droplets: $\chi_{i,j} = \frac{1}{i} + \frac{1}{j}$ or $\chi_{i,j} = \frac{1}{i^2} + \frac{1}{j^2}$ for the two mentioned mechanisms of droplet diffusion, respectively.

The formulation of problem for the coalescence related evolution of the ensemble of droplets on the surface of substrate during the rapid thermal annealing in normalised parameters allows one to simplify the simulation process. The kinetics of the evolution of the system of droplets in normalised parameters is determined only by the initial droplet distribution and annealing time, and does not depend explicitly on the annealing temperature and initial droplet density. Therefore, the use of the normalised parameters allows one to make only one run of simulations for every initial distribution function. The effect of annealing temperature and total droplet density can be then taken into account by respective time recalculations using formula (7) using the Arrhenius dependence of D_0 on annealing temperature T : $D_0 = D_0^0 \cdot \exp\left(-\frac{E_D}{kT}\right)$, where k is the Boltzmann constant, E_D is the activation energy of diffusion process, and D_0^0 is the pre-exponential term, respectively.

Eq. (8) was solved numerically to study the kinetics of the evolution of the distribution function of droplets as a result of their coalescence during the rapid thermal annealing. The fourth order Runge-Kutta method has been applied. The applicability of this numerical method to the solution of Smoluchowski equation (8) was verified by comparing of simulation results for $\chi_{i,j} = 1$ and initial distribution function of droplets in the form $v_i = \exp(-i)$ with the exact solution for this problem

$$\text{upon time } v_i(t) = \frac{\exp\left(-\frac{i}{1+t/2}\right)}{(1+t/2)^2} \quad [26, 27].$$

The initial distribution functions of Au droplets on size were chosen Gaussians with varied widths, to study the effect of width on the evolution of droplet ensembles. The integrated initial droplet density prior to annealing was normalised to unity that allows easy analysis of its change during rapid thermal annealing. The centre of size distribution was chosen to be at $1.24 \cdot 10^6$ atoms that for the typical system of Au droplets on the Si substrate corresponds to the average droplet radius of 30 nm.

Atom evaporation model. This section describes the model of evaporation of atoms from the surface of droplets during the rapid thermal processing of droplet ensemble on the surface of substrate. The rate of atom evaporation is determined by the attempt frequency α_0 , the activation energy of desorption E_{des} , and the number of atoms on the surface of droplet n_i . The kinetics of atom evaporation is described by the Fokker-Planck equation as follows:

$$\frac{\partial v_i}{\partial t} = \frac{\partial}{\partial i} (\alpha_i v_i) \quad (9)$$

where the normalised values for droplet densities have been used as in the previous section and

$$\alpha_i = \alpha_0 n_i \exp\left(-\frac{E_{des}}{kT}\right) \quad (10)$$

is the desorption rate of atoms, respectively.

Using the normalisation of time (see Eq. (7)) and taking into account the dependence of R_i and n_i on the number of atoms in the droplet i , Eq. (9) can be presented in the following form:

$$\frac{\partial v_i}{\partial \tau} = \lambda_0 \frac{\partial}{\partial i} (v_i \cdot i^{2/3}) \quad (11)$$

Eq. (11) was solved numerically by the second-order Lax-Wendroff method for different values of λ_0 .

Results and discussion

In this section, the results obtained in the framework of correlated evaporation/condensation droplet diffusion mechanism are presented. Qualitatively, the same results are obtained also for the periphery diffusion mechanism.

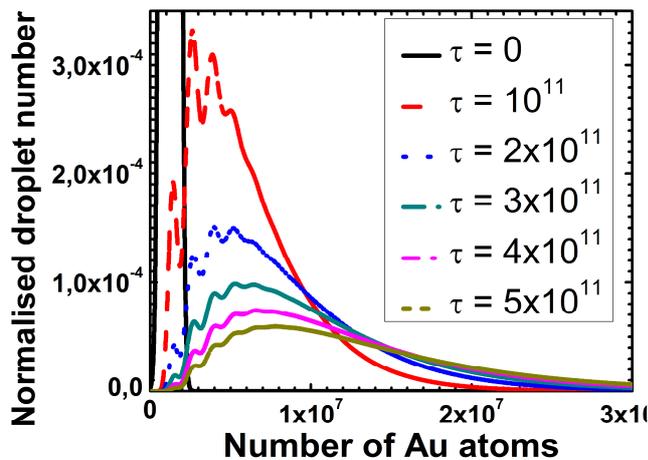


Fig. 3. Distribution functions of Au droplets for different moments of normalised time. Initial distribution width $\sigma = 3 \cdot 10^5$.

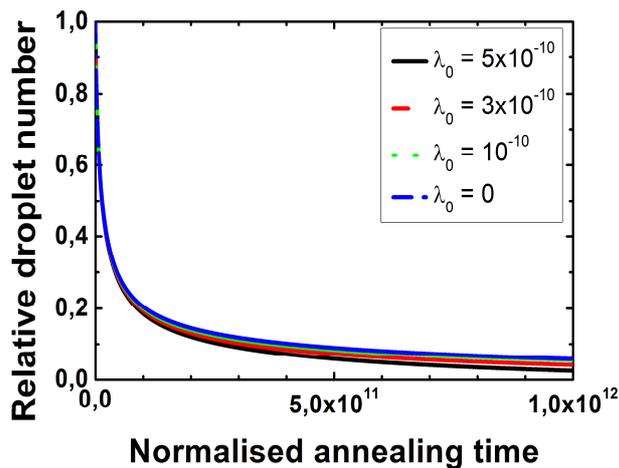


Fig. 4. Dependence of the relative value of droplets on the normalised time of rapid thermal annealing for different values of λ_0 .

In Fig. 3, the droplet distribution functions for different values of normalised annealing time are shown. As one can see in this figure, the distribution function broadens with time of RTA and its maximum shifts to the bigger sizes. The distribution function turns from Gaussian-like to logarithmic normal-like that is a typical behaviour for the coalescence related process [23, 24]. This process corresponds qualitatively to the experimentally observed behaviour of the distribution function of Au/Si droplets as reported in experimental section.

Fig. 4 demonstrates the dependence of the droplet number on the substrate surface on the normalised annealing time for different values of the evaporation rate of atoms from the droplets. The integrated droplet density decreases rapidly due to coalescence process and then tends to saturate. The saturation is likely caused by two reasons, namely: (i) the decrease of droplet mobility due to the increase of their size and (ii) the decrease of droplet number so that their collisions become less probable. The droplet density does not depend on the initial width of distribution function σ and changes only slightly with the evaporation rate at certain annealing time. Therefore, the principal action of evaporation from the surfaces of droplets consists in the decrease of droplet size. This mechanism affects only the smallest-size droplets contribution of which to the total droplet density is negligible.

Comparison with experiment. Fig. 5 shows the experimentally obtained dependence of the relative density of Au/Si droplets on the surface of Si substrate upon the temperature of rapid thermal annealing for the 3 nm Au film. Using the data presented in this Figure, the results of theoretical study were compared to the results of experiment as described below. The activation energy of the diffusion of Au/Si droplets on the surface of Si substrate was estimated.

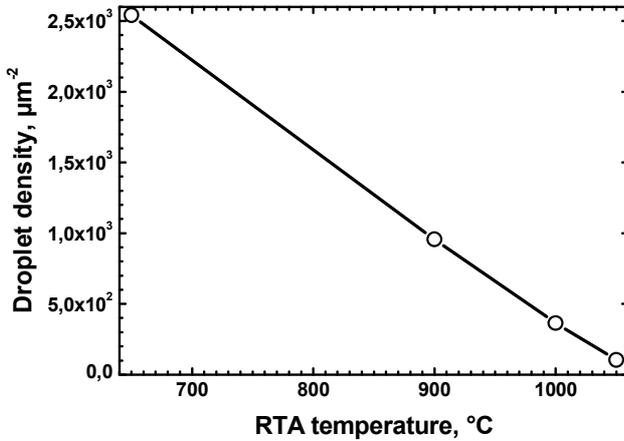


Fig. 5. Au/Si droplet density formed as a result of 20 s RTA treatment of 3 nm Au film on Si substrate versus treatment temperature.

droplets on the evaporation rate (see Fig. 4). From the curve of the calculated dependence of relative droplet density on the normalised time of annealing, the normalised time values τ_0 corresponding to the experimentally observed normalised grain densities were determined for different RTA temperatures.

Using the normalisation condition for time (7), the activation energy of the diffusion of droplets and the normalised time values corresponding to the experimentally observed values of normalised droplet densities are related as follows:

$$\tau_0 \sim \exp\left(-\frac{E_D}{kT}\right) \quad (13)$$

where E_D is the activation energy of droplet diffusion as introduced above.

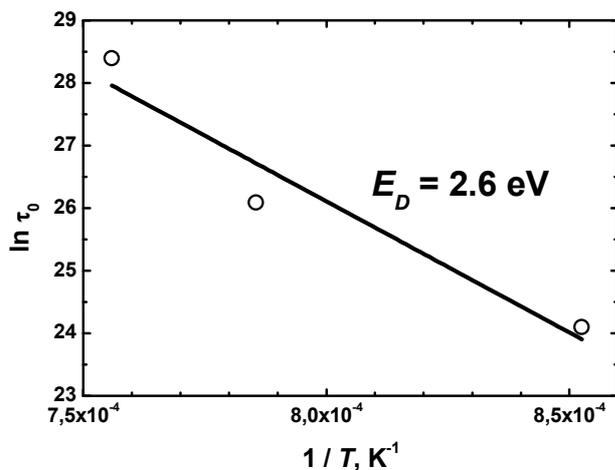


Fig. 6. Experimental dependence of the relative density of Au/Si droplets on the surface of Si substrate on the RTA processing temperature.

We make our comparison assuming that the evolution of droplet array during the RTA at the temperatures 900°C and higher starts from the droplet array similar to that obtained after annealing at 650°C so that the droplet density formed at this temperature serves as the normalising quantity. We additionally assume that the annealing time is the same for all the temperatures used.

Our study is further based on the practical independence of the relative density of

droplets on the surface of Si substrates is estimated to be ~ 2.6 eV in the model of correlated evaporation/condensation mechanism of droplet diffusion. Changing the mean value of the initial distribution of droplets on size, the E_D from ~ 2.4 up to ~ 3 eV are obtained for correlated evaporation/condensation mechanism and around ~ 2.7 eV for the periphery diffusion mechanism of droplet diffusion, respectively. The activation energy of droplet diffusion has reasonable estimated values, which are determined by a combination of the initial distribution of droplets as well as the actual mechanism of droplet diffusion on the surface of Si substrate.

Conclusion

In this work, the kinetics of the evolution of the distribution function of droplet arrays on the surface of substrates as a result of their coalescence and evaporation is considered. The total density of droplets for the initial distribution studied is mainly determined by the coalescence process, while the droplet evaporation leads to the decrease of the average droplet size. The coalescence leads to the transformation of the initial symmetrical Gaussian distribution function in the non symmetrical logarithmic-normal like with the time of annealing.

The results of theoretical study are compared to the experimental results on the evolution of Au/Si droplet arrays on the surface of Si substrate obtained as a result of RTA treatment at temperatures 900°C and higher. The activation energy of the diffusion of droplets are estimated from this comparison to be in the range of ~ 2.4 to 3 eV depending on the initial droplet distribution and their diffusion mechanism.

Acknowledgement

This work has been carried on in the framework of the STCU project #4080 “Development of an array of QNEM structures”.

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