Nucleation of CdSe thin films: the kinetic model

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Abstract. The growth of CdSe thin films by the method of thermal evaporation is studied. The growth model is developed and kinetic nucleation theory is applied to describe main dependencies of CdSe formation. Two mechanisms of growth are considered: 2D-growth (nucleation of disk-shaped nanoislands) and 3D-growth (nucleation of hemispherical nanoislands). The impact of growth conditions such as the substrate and evaporator temperatures and partial pressures on the nucleation mechanism is discussed. The conditions at which each mechanism prevails are estimated.

1. Introduction

In present time a lot of attention is paid to the growth technology of bulk semiconductor crystals and thin films. One of the major research areas are compound semiconductors of group AII-BVI, such as cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium selenide (CdSe) and many others. The main interest in these materials is based on their optoelectronic properties and possible applications in solar cell industry, radiation detectors, photoconductors [1-3]. CdSe is one of prominent semiconductors due to its high photosensitive properties and it is widely used in production of thin film transistors, detectors of gamma rays and PEC cells [4]. It is usually having n-type of conductivity and direct bandgap of 1.74 eV, which is suitable for visible light conversion. Due to great importance of this material in industry, it is very topical to study principles and mechanisms of formation of CdSe crystals, thin films and quantum dots. There are many techniques to grow CdSe, such as vacuum evaporation, pyrolysis, hot wall deposition, cathodic electrodeposition and many others [5-7]. The vacuum evaporation is quite simple and doesn’t require high material costs and thus will be considered in this paper. The other important question is the substrate, on which the film will be grown. In [6,8,9] authors have shown the advantages of use of SiC/Si structures, grown by the method of substitution of atoms [10], as substrates for growth of AII-BVI semiconductors. The main advantages are: accessibility of Si substrates, cheapness of formation of SiC/Si by the method of atom substitution, chemical stability of SiC film against precursors used in production of AII-BVI thin films, and a feature of method [10], namely the presence of pore system under the SiC film, which allows one to overcome stresses arising due to mismatch of crystalline lattices of CdSe, SiC and Si, and difference in their coefficients of thermal expansion.
Despite the numerous accumulated experimental data, as far as we know, there is no quantitative theory of formation of CdSe films by the method of vacuum evaporation. This paper is devoted to the study of CdSe formation mechanisms using nucleation theory, which would allow estimating of various parameters of the resulting films depending on growth conditions: temperatures of the evaporator and the substrate. The paper is the continuation of series of articles on the growth of AII-BVI semiconductors [6,8,9] on SiC/Si substrates.

2. Growth of CdSe thin film via vacuum evaporation

The process of growth of CdSe films by the method of evaporation and condensation in vacuum [6] was extensively studied by Kalinkin et. al [7] and is very similar to the growth of CdTe, described in [8,9]. During the growth CdSe powder is being heated up to the temperature $T_g$ in evaporation zone of the reactor. $T_g$ must be high enough to ensure sublimation of CdSe and its dissociation into molecules of Cd and Se$_2$ due to chemical reaction:

$$2\text{CdSe}(s) = 2\text{Cd}(g) + \text{Se}_2(g)$$

In current consideration we neglect formation of single Se atoms in vapor phase, since this process is not very probable. After sublimation Cd and Se$_2$ are being transferred to the substrate zone, which is heated up to temperature $T_s$, which is lower than $T_g$. Since the pressure of vapor is equal to saturated one at temperature $T_g$, a flux of components towards the surface exceeds the flux of components evaporating from the surface of the substrate. This causes accumulation of the material at the surface of the substrate and therefore growth of the film. There are several mechanisms of crystal growth such as growth by Burton, Cabrera and Frank mechanisms (moving of individual steps and growth spirals [11]), nucleation and growth of 2D disk-shaped nanoislands of monoatomic height, and nucleation of 3D-nanoislands having a shape of hemisphere or faceted surface (see Figure 1). Since at typical growth conditions difference in $T_g$ and $T_s$ is quite big to ensure high growth rates of the film, we assume that the growth mechanisms are mainly 2D- and 3D-nucleation. Growth via BCF mechanism is typically observed when supersaturation is small (<1-5%) and thus we will not consider it in current paper. It is quite important to understand which mechanism plays a dominant role: 2D or 3D-nucleation. During the growth in 3D-regime usually one can observe higher density of defects, grain boundaries, dislocations, and in some cases it allows growing different 3D-structures like quantum dots or nanowires. Nucleation in 2D-regime allows one to grow more homogeneous and smooth films, although at a slower growth rates.

Figure 1. Nucleation of adatoms into disk-shaped particles in 2D-regime (a) and into hemispherical particles in 3D-regime (b).
Below we will estimate conditions at which 2D- and 3D-nucleation take place during the growth of CdSe film [6]. We consider three main parameters which may affect nucleation: the adsorption energies of Cd and Se atoms (in this paper we suppose that Se₂ molecules are being completely dissociated into atoms on the surface of the substrate and diffuse across it, however one should note that another mechanism may take place at elevated temperatures, namely re-evaporation of Se₂ molecules and its transfer through gas phase across the substrate towards the growing particles [12], this mechanism will be studied in next papers); diffusion coefficients and, as a consequence, the mobility of Cd and Se adatoms, and supersaturation, which is determined by difference in the fluxes to/from the surface (temperatures $T_g$ and $T_s$).

3. Nucleation of CdSe film: model, parameters and results

To estimate which mechanism, 2D- or 3D-nucleation plays a key role one should calculate growth rate independently via both mechanisms at given conditions and compare them. In this section we describe the model, necessary parameters and calculation procedure.

We assume, that both types of adatoms (Cd and Se) diffuse independently and nucleate into nanoislands of CdSe according to:

$$\text{Cd(ad)} + \text{Se(ad)} = \text{CdSe(s)}$$

Nucleation rate $I$ can be calculated using equation [9]:

$$I = N_0 W^+(n_c) Z \exp(-\Delta F(n_c)/kT)$$  \hspace{1cm} (2)

where $N_0 \sim 1/l_0^2$, $n$ is the number of CdSe molecules in the nanoisland, $n_c$ is the number of CdSe molecules in critical nuclei, $Z$ is Zeldovich factor, $W^+(n_c)$ is the diffusion coefficient of the island in the space of sizes [9],

$$W^+(n_c) = -\frac{kT d\ln n}{d\Delta F/dn} \bigg|_{n=n_c}$$

$\Delta F(i)$ is the free energy of nuclei formation. For $\Delta F$ in case of 2D nucleation (disk-shaped nanoisland) one can write:

$$\Delta F(i)_{2D} = \alpha_{2D} n^{1/2} - \Delta\mu n,$$

and for the case of 3D nucleation (hemispherical nanoisland):

$$\Delta F(i)_{3D} = \alpha_{3D} n^{2/3} - \Delta\mu n,$$

where $\Delta\mu = kT \ln(C_{CdC_{Se}}/K^{eq}) = kT \ln(\xi + 1)$, $C_i$ are the concentrations of Cd and Se adatoms on the substrate surface; $K^{eq} = C_{Cd}^{eq}C_{Se}^{eq}$ is the equilibrium constant of the chemical reaction $\text{Cd + Se} \rightarrow \text{CdSe}$, $C_i^{eq}$ is the equilibrium concentration of the $i$-th element, $\xi = C_{CdC_{Te}}/K^{eq} - 1$ is the supersaturation of 2D gas of adatoms, $\alpha_{2D} = 2\pi^{1/2} \gamma(h\Omega)^{1/2}$, $\alpha_{3D} = (2\pi)^{1/3}(3\Omega)^{2/3}\gamma$, $\gamma$ is the effective surface energy of the island grains, $\Omega$ is the volume of the CdSe molecule, $h$ is the height of the island (equals to height of monolayer in our case). Using the results presented in [9] and the same chain of transformations one can write equations for nucleation rates in 2D case and in 3D case.
\[ I_{2D} = \frac{N_0^2 D_{CdSe} \Delta \mu^{3/2}}{\gamma (h \Omega kT)^{1/2}} \exp \left(- \frac{\alpha_2 D}{4kT \Delta \mu} \right), \]

\[ I_{3D} = \frac{N_0^2 D_{CdSe} \Delta \mu^2}{2^{3/2} \Omega (kT \gamma)^{1/2}} \exp \left(- \frac{4 \alpha_3 D^3}{27kT \Delta \mu^2} \right), \]

where \([12]\):

\[ D_{CdSe} = \frac{D_{Cd} D_{Se} C_{Cd}^{eq} C_{Se}^{eq}}{D_{Se} C_{Se}^{eq} \ln(\lambda_{Cd}/r_c) + D_{Cd} C_{Cd}^{eq} \ln(\lambda_{Se}/r_c)}, \]

\(\lambda_i\) is diffusion length of \(i\)-th adatom, \(r_c\) – is the critical radius of the nuclei.

In order to calculate growth rates numerically one have to determine firstly all abovementioned parameters, e.g. Cd and Se diffusion coefficients and lifetimes. These quantities can be determined the following expressions \([9]\):

\[ \tau_i = \tau_{0i} \exp \left( \frac{E_{a,i}}{kT} \right), \]

\[ D_i = \frac{l_i^2 v_i}{z} \exp \left( - \frac{E_{d,i}}{kT} \right), \]

where \(E_{a,i}, E_{d,i}\) are the activation energies of adsorption and diffusion of the \(i\)-th element, respectively, \(\tau_{0i}\) is inversely proportional to the frequency of vibrations of adatom \(v_i\) which equals to \(\sim 10^{13} \text{s}^{-1}\) \([9]\), \(l_i\) is the diffusion jump distance, which is for simplicity equals to lattice parameter of CdSe in our calculations \((l_i = 0.608 \text{ nm})\). \(z\) is the number of possible neighbor sites to which adatom can jump.

The activation energies of adsorption and diffusion of Cd and Se were chosen according to \([13]\), \(E_{a,Cd} = 0.3 \text{ eV}, E_{a,Se} = 2.07 \text{ eV}, E_{d,Cd} = 0.21 \text{ eV}, E_{d,Se} = 0.17 \text{ eV}\). Using this values and equations (1) and (2) one can calculate dependence of lifetimes, diffusion coefficients and diffusion lengths \((\lambda_i^2 = D_i \tau_i)\) on temperature. The results are presented in Figure 2.

Figure 2. The dependence of Cd and Se lifetimes and diffusion coefficients on the substrate temperature.
The second step is to determine equilibrium concentrations of Cd and Se adatoms at the surface, fluxes of atoms from vapor phase $J_{Cd}$ and $J_{Se}$ to the substrate, and to find supersaturation $\xi$ depending on temperature of the substrate $T_s$ and the evaporator $T_g$. To do so we can use the data on the saturated vapor pressure of Cd and Se$_2$ over the surface of congruently sublimating crystal of CdSe [14], which can be described by the formula $\log P_{Cd}(\text{atm}) = -11138.7 / T + 6.91$. We also assume that $P_{Cd} = 2P_{Se_2}$. Using the data, one can calculate fluxes of Cd and Se to the substrate: $J_{Cd} = P_{Cd}/(2\pi m_{Cd} kT)^{1/2}$ and $J_{Se} = 2P_{Se_2}/(2\pi m_{Se_2} kT)^{1/2}$, correspondently, where $m_{Cd}$ and $m_{Se_2}$ are the masses of Cd and Se$_2$, correspondently. After the flux densities are calculated, it is easy to estimate the adatom concentrations using the formula $C_i = n_i/N_0 = J_i t_i/N_0$, where $n_i$ is the surface density of the $i$-th adatom [9]. Surface energy or CdSe $\gamma$ equals to 0.246 $J/m^2$ [13].

Thus we have a full set of data to perform calculation of nucleation rates via different mechanisms: 2D and 3D (equations 3,4). We performed calculation of $I_{2D}$ and $I_{3D}$ at different temperatures of the evaporator and the substrate. To determine, which mechanism plays the key role, we build the ratio of $I_{2D}/I_{3D}$, which is shown in Figure 3. Dashed white line denotes conditions at which $I_{2D} = I_{3D}$.

![Figure 3](imageurl) Figure 3. The dependence of the ratio $I_{2D}/I_{3D}$ on the temperatures of the evaporator and the substrate. Dashed line marks region at which ratio $I_{2D}/I_{3D}$ equals to 1. Dash-dotted line marks equality of temperatures $T_g$ and $T_s$.

There are 4 regions in the Figure 3. The region denoted as I corresponds to growth mainly via 3D nucleation of hemispherical CdSe nanoislands ($I_{2D} \ll I_{3D}$). This regime ensures higher growth rates in more nonequilibrium conditions, which may lead to formation of various defects like boundary grains, dislocations etc. In addition, it is possible in this regime, that other three-dimensional structures, such as filamentary crystals or nanoislands of more complex shape will also be formed. The regime denoted as II corresponds to growth mainly via 2D nucleation of monolayer-height disk-shaped nanoislands of CdSe ($I_{2D} \gg I_{3D}$). This regime can be characterized as layer-by-layer growth in more equilibrium conditions, and in this regime smoother films with less number of defects will grow. The region denoted
as III corresponds to extremely small nucleation rates via both mechanisms and it seems that growth should occur via different growth mechanisms (e.g. Burton-Cabrera-Frank). The region denoted as IV corresponds to sublimation of the crystal, since substrate temperature $T_s$ is higher than $T_g$.

4. Conclusions

The growth of CdSe via the method of evaporation and condensation in vacuum is considered. The model of growth is proposed based on nucleation theory of multicomponent systems. Estimates of the parameters of the model at different temperatures of the evaporator and the substrate are made (supersaturation, equilibrium concentrations, Cd and Se adatoms lifetimes, diffusion coefficients and lengths). Calculations are performed for the nucleation rate of CdSe nanoislands of different shapes (hemispherical and disk-shaped) and it is shown that there are two regimes at which nucleation of certain type of nanoislands prevails. The calculations presented open up new possibilities in controlling of growth rate and quality of CdSe thin films and nanostructures by the method of thermal evaporation and condensation in vacuum. The method proposed can be used also to study growth of other types of crystals and thin films.

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