Deposition rate effect of Alq3 on ITO surface: A Kinetic Monte Carlo study

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Abstract

Organic thin film of aluminum tris (8-hydroxyquinoline) (Alq3) were evaporated on the indium tin oxide (ITO) coated glass substrates under different deposition rate condition. In this research, the effect of deposition rate on the surface morphology of top Alq3 films is studied. In order to investigate the deposition rate effect of Alq3 thin film, AFM image was used to study the characteristic of surface morphology and surface roughness. In simulation segment, we use Kinetic Monte Carlo (KMC) technique to simulate the thin film growth with a 3D growth model. The result shows that the surface presents a smooth morphology which contains large and short islands when deposition rate is low. But the surface morphology proceeds with rough morphology which contains lots of small islands for high deposition rate. The deposition rate is identified as one of the key factor in the deposition Alq3 molecules to ITO surface due to its great influence on the surface morphology of top Alq3 films.

Keyword:
KMC, step-flow growth, step-edge, temperature effect, step-width effect, diffusion length, transition temperature

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Introduction

Spontaneous patterning is a well-known issue of surface morphology in thin film growth process, mostly due to the step instability [1]. The step instability, such as bunching [2-5] and meandering [6] during step-flow growth, induces the pattern formation on the surface of semiconductor and metal [2-6]. The step-flow growth during homoepitaxial deposition produces various step patterns spontaneously, as found on the vicinal surface of metal Cu [7] or semiconductor Si [1,8,9] and GaAs [10,11]. Step-flow growth is a growth mode with the adatoms diffusing directly to the step-edge instead of nucleating on terrace. The kinetics of adatoms at step-edge or on terrace is therefore our major concern in this study.

According to the experimental results presented by Zilani et al [12], there exist significant differences among growth morphologies of clusters observed on surfaces in terms of shape, size and terrace width. It is shown that diffusing adatoms experience an additional barrier, so-called Ehrlich-Schwoebel (ES) barrier to incorporate into surface at step edges [13]. However, the adatoms prefer to attach to the step-edges of the terrace which they deposit, rather then attach to those steps belong to the terrace above them. Bales and Zangwill have shown that the step instability can be ascribed to an asymmetry in attachment at step edges due to the ES barrier [14]. Kinetic Monte Carlo (KMC) technique has been employed to simulate the silicon growth with a 2D solid-on-solid (SOS) model and can provide solid evidences for the presence of step bunching in an asymmetric step-edge barrier with the behavior of an inverse type ES barrier (iES) [3,4]. Vilonel et al have demonstrated that nucleation and step-edge barrier can destabilize step-flow growth with a vicinal surface [15]. The ES barrier for interlayer diffusion has been identified as the main factor to determine three-dimensional growth modes [13,16]. Extensive studies were devoted in investigating the step instability including faceting, step bunching and step
meandering during step-flow growth induced by either thermodynamic or kinetic effects on the substrate [17-20]. H. Minoda investigated the step instability on Si surface induced by the direct current (DC)-heating effect and step bunching induced by metal absorption by reflection electron microscopy (REM) and optical microscopy [1]. Recently, H. Omi showed that, during step-flow growth, there existed three different types of step bunching and each of them is with a characteristic temperature range and specific morphology of the step pattern [21].

Diffusion length is highly related to the aggregation of adatoms at step-edge and is also a key factor to cause the step-instability. The step-instability, such as bunching and meandering during step-flow growth, induce the pattern formation on the surface of semiconductor and metal [1-6]. It is rather interesting that, during the step-bunching, the wide terraces tend to broaden and produce the well-known ripple formation on the semiconductor-like surface [4]. As a result, the diffusion length of adatoms in producing a step-down mass current is therefore the major concern in this study. We investigated the diffusion length of adatoms on a semiconductor-like uniform-spacing stepped surface. In order to find out the relation between diffusion length \((R)\) and half of step-width \((L/2)\), the simulation model was established with iES barrier in various substrate step-widths (step-width effect) and substrate temperatures (temperature effect). Our approach is the following. Firstly, in order to facilitate the prediction of the growth pattern on surface, the relationship between diffusion length \((R)\) and half of step-width \((L/2)\) was utilized to estimate the transition temperature \(T_c\) between the growth modes. Secondly, the influence of step-width on surface growth mode around the transition temperature region was investigated. Finally, a step-width temperature diagram was constructed to characterize the surface growth mode.

**Model and method**
**Model:**

In the simulations, both deposition and diffusion of adatoms on the substrate surface are considered as elementary processes. In this study, we investigated the diffusion length of adatoms and neglected the adsorptions from the surface. A 100x100 lattice was used as the basic substrate, which can be treated as one step, and this substrate can be further divided into several steps with equal width, including 2 steps (50 atoms per step) • 4 steps (25 atoms per step) • 5 steps (20 atoms per step) • 10 steps (10 atoms per step) and 20 steps (5 atoms per step) as shown in Fig. 1. The deposition rate is set as 0.7 monolayer per second (ML/sec). The deposition time is one second and therefore the total deposition atoms are only 7000 atoms. Because the thickness in each step is only one monolayer, the SOS model [22-28] can be used as the simulated system without defect. This substrate system can simulate a simple cubic crystal with a regular facet [100]. Periodic boundary condition is applied along the x-axis and y-axis in the model as shown in Fig. 2a, with the step-flow direction as y-axis.

**Method:**

The growth process is described by random deposition on the substrate with a constant rate. The transition rate for a diffusion process from lattice site $i$ to $j$ is assumed to be

$$\nu = \nu_0 \exp\left(\frac{E^{ij}}{k_B T}\right)$$

(1).

The diffusion rate of adatoms is assumed as Arrhenius type, where $\nu_0$ is the atomic vibration frequency which is assigned as

$$\nu_0 = \left(\frac{2K_B T}{h}\right)^{\frac{1}{2}}$$

(2),

where $T$ is the substrate temperature and $k_B$ is Boltzmann constant. The activation energy $E^{ij}_a$ is determined by a bond counting scheme with
$E_A^\prime = E_S + nE_N + E_{\text{step}}$ \hfill (3),

where $E_S$ is the surface potential; $n$ and $E_N$ are the number of the nearest neighbors and the binding energy between any two nearest neighbors, respectively. $E_{\text{step}}$, so-called step-edge barrier, is the anisotropic diffusion (iES barrier) for an atom hopping from the current step to the edges of the upper step. These energy potentials are shown in Fig. 2b and the typical semiconductor parameters [3] is set as $E_S = 1.0eV$, $E_N = 0.25eV$ and $E_{\text{step}} = 0.15eV$, respectively. By adjusting the step-edge barrier, we can describe the asymmetric step-edge barrier suggested by Schwoebel et al [29-30].

The diffusion length ($R$) can be estimated by Einstein diffuse equation in homogeneous diffusion as shown in Fig. 3

$$R^2 = 4D\text{t}$$ \hfill (4),

where $D$ is diffusion coefficient with the unit (length$^2$/Sec) and $t$ is the time elapse between two consecutive atomic deposition events. The diffusion coefficient can be calculated by $D = AV_0 \exp\left(-\frac{E_A}{kT}\right)$ where $A = n_x \cdot n_y \cdot a^2$, and $n_x$ and $n_y$ are the average diffusion distance along $x$ and $y$ axes and $a$ is the lattice constant.

In order to characterize the surface morphology of step-flow growth, two analytical methods are used to discuss the simulation results: step growth coverage ($SGC$) and step-flow analysis. The $SGC$ can be expressed as

$$SGC = \frac{N_{\text{step}}}{N_{\text{total}}}$$ \hfill (5),

where, $N_{\text{total}}$ is total numbers of deposition atoms and $N_{\text{step}}$ is the number of atoms flowing across steps boundaries. Step-flow analysis includes two parameters, average step-flow layer ($SFL$) and step-flow ratio ($SFR$), to characterize the pattern formed by the adatoms on the step edges. $SFL$ describes the average number of layers per step, formed through the step-flow growth. $SFL$ and $SFR$ are defined as

$$SFL = \frac{N_{\text{step}}}{(\text{number of steps} \times L_0)}$$ \hfill (6),
where $L_x$ is the width of the substrate in $x$ direction. By combining the SFL with the width of step, $SFR$ represents average step-flow covering, i.e., the expansion ratio for each step as shown in Eq. (7).

**Result and Discussion**

In order to investigate the variation in the diffusion length ($R$) of adatoms, which induces the change in surface morphology, we studied the temperature and step-width effects, and summarized these two effects with a phase diagram.

**(A) Temperature effect**

By comparing the diffusion length ($R$) with half of step width ($L/2$, $L$ is step width), we can elucidate the relation between temperature effect and surface growth mode. We roughly divide temperature range into three regions including T1 region (300K–500K), T2 region (500K–750K) and T3 region (750K–1000K) according to the growth morphology. In the simulation scheme, the temperature parameter is implemented in the Arrhenius equation which is used to calculate the diffusion rate. When temperature raises, the average kinetic energy of adatoms increases; the diffusion rate and length of adatoms also increase and therefore the adatoms can diffuse to a more stable position with more neighboring adatoms. If temperature is high enough, the adatoms with large $R$ can easily diffuse from the initial deposition position to the step-edge (Fig. 3) and enhance the step-flow. From the Arrhenius and Einstein diffusion equation (Eq. 4), $R$ is dependent only on temperature and therefore we can investigate the temperature effect on step-flow growth through the relationship between the $SGC$ and $R$, since $R$ depends only on temperature. The results are listed in Table 1. Since $L/2$ can be used to characterize the range of homogeneous diffusion, we can further explore the temperature effect through the relationship between $R$ and
L/2 with the results of SGC simulation. As listed in Table 1, it shows that the SGC values increase as temperature increases. When temperature belongs to T1 region (300K~500K), most of the adatoms stay at the original random deposition site due to lack of enough kinetic energy to diffuse and therefore the morphology belongs to random deposition growth. When temperature raises gradually to T2 region (500K~750K), the $R$ of adatoms increases accordingly and homogeneous diffuse appears. The step-flow appears only when $R$ is compatible to $L/2$ for systems with narrow step-width in T2 region. The step-flow morphology becomes apparent because that around 750K there are over 50% ($SGC > 0.5$) of adatoms diffusing to the step-edge. When $L/2$ decreases with temperature fixed the $SGC$ increases. When temperature belongs to T3 region (750K~1000K), $R$ is longer than the largest step-width in our models (50 atoms per step), and the $SGC$ increases substantially over 50%. When temperature reaches 1000K, there are over 90% of adatoms contributing to step-flow growth and the surface morphology is composed entirely by step-flow growth.

The $SGC$ values are almost close to zero when $L/2$ is larger than $R$ value and the $SGC$ values become substantial if $L/2$ is equal or smaller to $R$ value. The increasing of the $SGC$ value can be used to depict the onset of step-flow growth. Thus, the growth mode can be characterized according to relation between $R$ and $L/2$, as shown in the following.

\[ R \leq 1 \quad : \quad \text{Morphology proceeds with random deposition mode}; \]
\[ 1 < R < \frac{L}{2} \quad : \quad \text{Morphology proceeds with island mode}; \]
\[ R \geq \frac{L}{2} \quad : \quad \text{Morphology proceeds with step-flow mode}. \]

When $R \leq 1$, most of the adatoms stay at the initial random deposition site. When $1 < R < \frac{L}{2}$, the adatoms tend to diffuse around within the step terrace, and step-flow
growth is not pronounced. But when $R \geq \frac{L}{2}$, the diffusion length can cover the entire step-width, so the adatoms tend to attach to the step-edge and the step-flow growth become apparent. As a result, the step-flow growth becomes the dominant growth mode. The $SGC$ results of these simulations are plotted in Fig. 4. In T1 region (below 500K), the value of $SGC$ is close to zero and $R$ of adatoms is smaller than $L/2$ due to low kinetic energy and only few adatoms near the step-edge. As shown in Table 1, diffusion lengths are smaller than 1 when temperature is below 500K. With $R \leq 1$, the adatoms are unable to diffuse on the surface and this makes the surface morphology mainly composed by random deposition growth. As temperature increases over 500K, the adatoms start to aggregate around the step-edge and the pattern of the step-flow growth emerges.

The analyses of $SFL$ and $SFR$ also yield the similar conclusion but can provide with more detail information in terms of the adatoms diffusion between steps, as shown in Table 2. For example, when temperature reaches T2 region (500K~750K), the aggregation near the outer step-edge is mainly formed by the adatoms from the upper step and a few from the lower step (anisotropic diffusion for iES barrier), as shown in Fig. 3. The adatoms tend to gather near the step-edge with high neighboring numbers and induce the step-flow growth. In T3 region (750K~1000K), the aggregation near the outer step-edge is mainly formed by the adatoms from both the upper and lower steps. When temperature reaches 1000K, there are over 90% of adatoms gathering at the step-edge with $SFR$ up to 64%.

(B) Step width effect

From the above discussion, it is found that the ratio between $R$ and $L/2$ can determine the pattern of surface morphology. Since $R$ is only dependent on temperature (Eq. 4), one can characterize the step-width of the substrate with a
transition temperature \( (T_c) \) for the onset of step-flow growth, i.e., when \( R \) is equal to the \( L/2 \), as shown in the previous section. The relation between the \( T_c \) and \( L/2 \) for all simulation models are shown in Table 3. It is found that the model with narrow step-width corresponds to low \( T_c \). With narrow step-width, the adatoms can easily aggregate to the outer step-edge through homogeneous diffusion, and make the onset of step-flow growth appear even in low temperature. Therefore, \( T_c \) is low for the model with narrow step width (\( T_c = 537 \text{K} \), for step width: 5 atoms). However, with wide step-width, the aggregation through island growth on the terrace competes with the cluster formation around the step-edge and therefore temperature has to increase to allow the adatoms to diffuse far enough to be able to attach the outer step-edge. For example, \( T_c \) is 676K for substrate with 50 atoms as step-width, and \( T_c \) is 572K for substrate with 10 atoms as step-width.

As shown in Fig. 5, the \( SGC \) decreases as the step width increases at almost all the temperature. It is interesting to note that the step-width effect is not pronounced in T1 and T3 regions. In T2 region, the step-flow growth is strongly influenced by step width. By combining the simulation results in Fig. 5 with \( T_c \) in Table 2, it is found that when temperature is larger than \( T_c \), step-down mass current appears and the step-flow growth begin. In T2 region, the \( T_c \) increases as the step-width increases. When temperature is larger or lower than \( T_c \), the trend of \( SGC \) is not evident and this indicates that the surface growth mode is not influenced by the step-width effect in these temperature regions. The influence of the step-width effect becomes noticeable on surface growth mode when temperature is in T2 region since the transition temperatures of all the studied models in T2 region. It is because that the surface growth pattern is determined by the competition between the island formation and step-flow growth in this temperature region and therefore it is rather sensitive to the variation of step-width. In order to demonstrate the extent of step-flow growth
influenced by step-width effect, we compare the SFR with various step widths as shown in Table 2.

(C) Phase diagram discussion

Combining the results of previous two sections, we constructed a phase diagram (see Fig. 6 for details) to explain the surface growth mode. We divided the phase diagram into three different regions according to SGC value: Region I (SGC: 0~0.125), Region II (SGC: 0.125~0.87) and Region III (SGC: 0.87~1). The surface growth mode in Region I belongs to random deposition growth. Judging from simulated morphology shown in Fig. 7 (300K), the deposition growth is the dominant mode in Region 1 and surface growth pattern shows minimal influence by either temperature or step-width effects. In Region III, the surface growth mode belongs to step-flow growth and is not influenced by either temperature or step-width effects. As a result, we can conclude that the surface growth mode is not affected by step-width effect when temperature belongs to T1 and T3 regions.

Comparatively, the SGC varies at Region II as shown in Fig. 6. The Region II represents the transition from random deposition growth to step-flow growth. The black curve in Region II represents the $SGC = 0.5$. The black dots below the black curve represent the $T_c$ points. The results show that $T_c$ increases as step-width increases. The black curve of $SGC$ rises slowly as step-width increases. Generally speaking, by increasing temperature or decreasing step-width, the surface morphology is dominated by step-edge aggregation and this in turns makes the step-flow growth apparent.

Conclusion:

We successfully analyzed the influence of temperature and step-width on the surface growth pattern of a semiconductor-like uniform-spacing stepped model with
inverse Ehrlich-Schwoebel (iES) barrier. The relation between diffusion length \(R\) and half of step-width \(L/2\) is constructed to estimate the \(T_c\) in order to predict the growth mode on the surface. A step width-temperature diagram was employed to characterize the surface growth mode into three regions, i.e., random deposition growth, step-flow growth and transition between these two growth modes, according to the step growth coverage and \(T_c\). It is found that the step-width effect has great influence on surface growth mode in the transition region. Our results not only shed a light on understanding the surface morphology controlled by the temperature and substrate topology, but also provide a simple way to predict the surface growth mode, which is crucial for the thin film growth process.

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**References**


