Vol 16 No 10, October 2007
1009-1963/2007/16(10)/3029-07

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Simulation of multilayer Cu/Pd(100) heteroepitaxial growth by pulse laser deposition*

Wu Feng-Min(吴锋民)†, Lu Hang-Jun(陆杭军),
Fang Yun-Zhang(方允樟), and Huang Shi-Hua(黄仕华)

Institute of Condensed Matter Physics, Zhejiang Normal University, Jinhua 321004*, China*

(Received 12 December 2006; revised manuscript received 16 March 2007)

The heteroepitaxial growth of multilayer Cu/Pd(100) thin film via pulse laser deposition (PLD) at room temperature is simulated by using kinetic Monte Carlo (KMC) method with realistic physical parameters. The effects of mass transport between interlayers, edge diffusion of adatoms along the islands and instantaneous deposition are considered in the simulation model. Emphasis is placed on revealing the details of multilayer Cu/Pd(100) thin film growth and estimating the Ehrlich–Schwoebel (ES) barrier. It is shown that the instantaneous deposition in the PLD growth gives rise to the layer-by-layer growth mode, persisting up to about 9 monolayers (ML) of Cu/Pd(100). The ES barriers of 0.08 ± 0.01 eV is estimated by comparing the KMC simulation results with the real scanning tunnelling microscopy (STM) measurements.

Keywords: heteroepitaxy, pulse laser deposition, Ehrlich–Schwoebel (ES) barrier, kinetic Monte Carlo simulation
PACC: 6855, 6840, 6890

1. Introduction

The morphology and growth mode of homoepitaxially and heteroepitaxially grown films depend dramatically on the thermodynamic properties of the film–substrate combination, as well as the kinetic parameters, such as surface misfit energies, diffusion barriers, deposition rate and surface temperature, etc.[1] There occur three kinds of growth modes during film formation, i.e. two-dimensional layer-by-layer (2D, Frank–van de Merwe) growth mode, three-dimensional (3D, Volmer–Webber) growth mode and 2D–3D (Stranski–Krastanov, S-K) growth mode.[2] In particular, the layer-by-layer growth is a quality of growth and highly desirable as it allows the preparation of structurally well-defined films.[3] It is known that pulse laser deposition (PLD) can lead to a better epitaxial growth than traditional thermal deposition (TD) in molecular beam epitaxy (MBE)[4,5] and keep layer-by-layer growth mode up to a few monolayers (ML) in thickness.[6−9] Although the structure properties of Pd/Cu(100) thin films and the phase transition from fcc to bcc structure for Cu/Pd(100) have been studied extensively,[10−13] detailed growth processes, especially the interlayer mass transport during multilayer heteroepitaxy of the two systems prepared by PLD, are not yet fully understood and need further investigation.

During the formation of multilayer thin films, the Ehrlich–Schwoebel (ES) barrier,[14−16] which is an additional barrier for atoms joining a descending step to overcome, plays an important role in the growth modes. The ES barrier is also described as the degree of interlayer mass transport during the growth of multilayer thin films. The ES barrier on the surface of different materials has been a subject of numerous theoretical studies.[17−22] In addition, several attempts have been made to evaluate the ES barrier from experimental data by using different approximations.[23−27] However, the ES barrier is still not known for a wide variety of systems, including the Cu/Pd(100) and Pd/Cu(100) heteroepitaxial systems, and it is difficult to calculate from first principles.

On the other hand, Kinetic Monte Carlo (KMC) simulations have been used with considerable success to model the essential features of epitaxial (homo- and hetero-) growths of metals as well as semiconductors,[28−34] such as simulations of multilayer Fe(100) homoepitaxy,[27] Si(001) homoepitaxy

*Project supported by the State Key Development Program for Basic Research of China (Grant No 2006CB708612) and Natural Science Foundation for Young Scientists of Zhejiang Province, China (Grant No RC02069).
†E-mail: wfm@zjnu.cn

with anisotropic sticking probabilities,[35] heteroepitaxies of Au/Ir(111) and Au/Pt(111),[36] and unstable epitaxy in systems with the ES barriers to interlayer diffusion.[37−40] Model parameters can be fitted by comparing with measurements, and in some cases it is possible to achieve quantitative or semi-quantitative agreement[41] and even to make predictions about the growth modes and material properties.

In the present work, the heteroepitaxially PLD grown multilayer thin films of Cu/Pd(100) are simulated by using KMC method with a realistic growth model and physical parameters. We concentrate on revealing the growth details during the formation of multilayer Cu/Pd(100) thin films and estimating the ES barrier of this system by comparing the KMC simulation results with the real scanning tunnelling microscopy (STM) measurements.

2. Strategy of modelling

The KMC simulation is based on solid-on-solid model with periodic boundary conditions and carried out on a 200×200 lattice. To simulate the instantaneous deposition in pulse laser deposition, the high deposition rate of 10^4 ML/s during the pulse, 34 ns pulse length and a repetition frequency of 5 Hz are set up, which are consistent with those in the real PLD experiments.[3,9] The deposited copper monomers are located at randomly chosen positions of the Pd (100) flat substrate. They are allowed to diffuse on terrace with a diffusion rate (Arrhenius form)

$$D_{\mathrm{d}} = D_0 \exp(-E_{\mathrm{d}}/k_{\mathrm{B}}T), \tag{1}$$

where E_{d} is the activation energy for monomers, T is the temperature and k_{B} is the Boltzmann's constant. They diffuse with the same prefactor $D_0 = 10^{12}$ s^{-1}. In the initial stage of Cu/Pd(100) growth, Cu adatoms diffuse onto Pd(100) surface with an activation barrier $E_{\mathrm{d}} = 0.73$ eV,[35] and then with another activation barrier $E_{\mathrm{d}} = 0.425$ eV diffuse onto Cu(100) surface.[42] In order to take into account an island relaxation, the rate of diffusion for atoms along the edge of an island is also included by assuming the rate of edge-diffusion to be

$$D_{\mathrm{e}} = D_0 \exp(-E_{\mathrm{e}}/k_{\mathrm{B}}T), \tag{2}$$

where E_{e} is the edge-diffusion barrier ($E_{\mathrm{e}} = 0.247$ eV for Cu adatoms[43]). When monomers diffuse to and arrive at a step, they will attempt to go down the step with an additional step-barrier energy (ES barrier) E_{es}, and the rate of interlayer diffusion is given by

$$D_{\mathrm{es}} = D_0 \exp\left[-(E_{\mathrm{d}} + E_{\mathrm{es}})/k_{\mathrm{B}}T\right]. \tag{3}$$

The ES barrier is defined as the difference between the energy barrier for an adatom to diffuse from a terrace to the layer below and the energy barrier for diffusion onto a flat terrace. The existence of this barrier has been shown to lead to a morphological instability.[44] Unfortunately, the ES barrier is still unknown for a wide variety of systems, and is difficult to calculate from first principles. We estimate the ES barrier in the multilayer growth of Cu/Pd(100) from the KMC simulation and compare it with the real scanning tunnelling microscopy (STM) measurements. The critical island size is set to be $i = 1$ at room temperature, i.e. dimers will not move any longer and form stable nuclei. The active monomers will stick to an island with a unit probability and diffuse along the edge of the island with a diffusion rate D_{e} and then become part of the island when they reach a site adjacent to it.

3. Results and discussion

In order to reproduce the morphologies of heteroepitaxial growth, a suitable ES barrier should be estimated first. We have taken the ES barrier as a variable parameter appearing in the diffusion rate in expression (3), and then calculated the surface roughness as shown, for example, in Refs.[27, 45], where the authors successfully simulated the re-entrant layer-by-layer growths of Fe/Fe(100) and Pt/Pt(111). The surface roughness is defined as[46]

$$w = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(h(x_i) - \bar{h})^2}, \tag{4}$$

where $n = 200 \times 200$, $h(x_i)$ is the height of thin film at the position of x_i and $\bar{h}$ is the average height of thin films, which is described as $\bar{h} = 1/n \sum_{i=1}^{n} h(x_i)$. A larger value of roughness corresponds to a morphology that has more layers simultaneously exposed to the surface. The oscillation of roughness with increasing coverage with a periodicity of 1 ML means the layer-by-layer growth mode, and the lowest value of roughness for each oscillation corresponds to an integral number of coverage. So the surface roughness can accurately determine the growth mode during thin film formation.

Figure 1 demonstrates the coverage dependence of surface roughness for different ES barriers at $T = 300\,\mathrm{K}$. It is clear that when $E_{\mathrm{es}} < 0.05\,\mathrm{eV}$, the growth mode is a complete layer-by-layer growth mode even the coverage reaches as high as 12 ML. When the ES barrier increases to 0.08 eV, the complete layer-by-layer (θ = 0–6 ML) and the nearly layer-by-layer growth mode remains up to 8–9 ML of coverage. Furthermore, when $E_{\mathrm{es}} = 0.10\,\mathrm{eV}$, the growth mode performs a complete 3D growth when the coverage $\theta > 3$–4 ML. In a way similar to that in Ref.[27], an ES barrier $E_{\mathrm{es}} = 0.08 \pm 0.01\,\mathrm{eV}$ can be estimated for Cu/Pd(100) heteroepitaxy by comparing the KMC simulation results with the experimental results.[9]

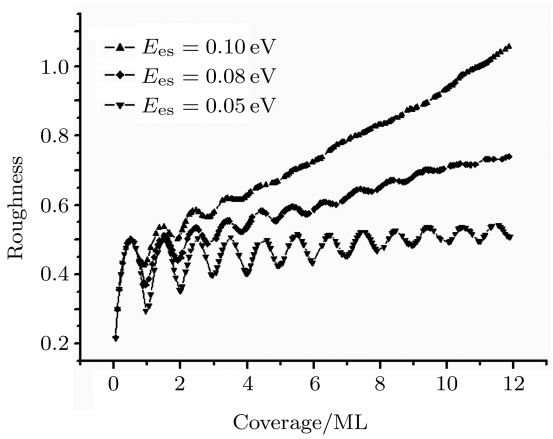


Fig.1. Coverage dependence of the surface roughness of the PLD Cu/Pd(100) heteroepitaxy for three values of E_{es} at room temperature.

For comparison, we have also prepared Cu films on the same Pd(100) substrate at the same substrate temperature (300 K) by thermal deposition (TD). The deposition rate was typically set to be 0.0017 ML/s. It means that there is the same number of adatoms deposited on the substrate as that in the PLD for the same deposition time. The coverage dependence of the surface roughness of the TD Cu/Pd(100) heteroepitaxy for three values of E_{es} at room temperature is shown in Fig.2. Clearly, in the TD case, when $E_{\mathrm{es}} = 0.08\,\mathrm{eV}$, the layer-by-layer growth mode persists up to only 3–4 ML, while it remains up to about 9 ML in the PLD case. Similar results for $E_{\mathrm{es}} = 0.05$ and 0.1 eV are also shown in this figure. It is evident that the PLD growth can improve the layer-by-layer growth significantly. This improvement on growth is due to the characteristic features of the PLD, in particular the extremely high instantaneous deposition rate. The detailed analysis will be given in the following sections.

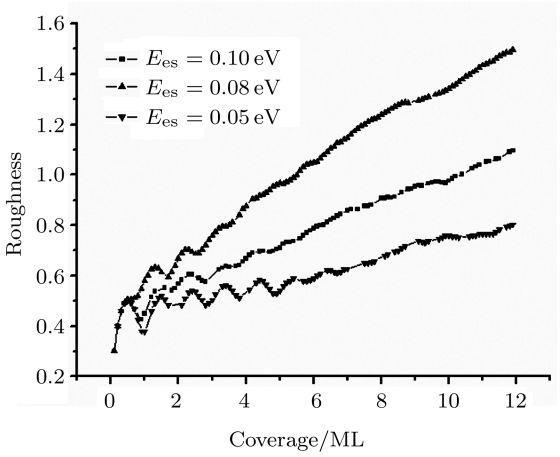


Fig.2. Coverage dependence of the surface roughness of the TD Cu/Pd(100) heteroepitaxy for three values of E_{es} at room temperature ($F = 0.0017$ ML/s).

Figure 3 describes the morphologies of Cu on Pd (100) thin film grown via PLD based on the KMC simulation at $T = 300\,\mathrm{K}$ and E_{es} =0.08 eV, where the coverages are set to be 0.85, 2.1, 3.05, 6.0, 9.0 and 12.0 ML, separately. At 0.85 ML as seen in Fig.3(a), the second layer nucleation is not found, and the effects of coalescence between islands and morphology percolation take place. In a thickness of 2.1 ML more than 95% of the second layer is accomplished and only a few islands remain in the third layer, while at 3.05 ML most of the third layer is filled. The layer-by-layer growth mode nearly persists up to a coverage of 6.0 ML. With increasing Cu thickness up to 9.0 ML, four layers appear simultaneously on the surface and the growth mode changes from nearly layer-by-layer to 3D multilayer growth one. When the thickness increases up to 12 ML, the growth takes place in a typical 3D mode, where more than five layers (from the 10th to 14th layers) are exposed on the surface. In contrast with the 3D growth in thermal deposition homoepitaxy of Cu/Cu(100) at room temperature,[40] the growth mode in the PLD heteroepitaxy of Cu/Pd(100) is a good layer-by- layer mode at the early stage ($\theta < 6$ ML) and via the 2D–3D (S-K) growth mode region (θ = 6–9 ML), it switches to a 3D growth mode at higher coverages ($\theta > 9$ ML).These simulation morphologies are consistent with those from the STM experimental images closely.[9]

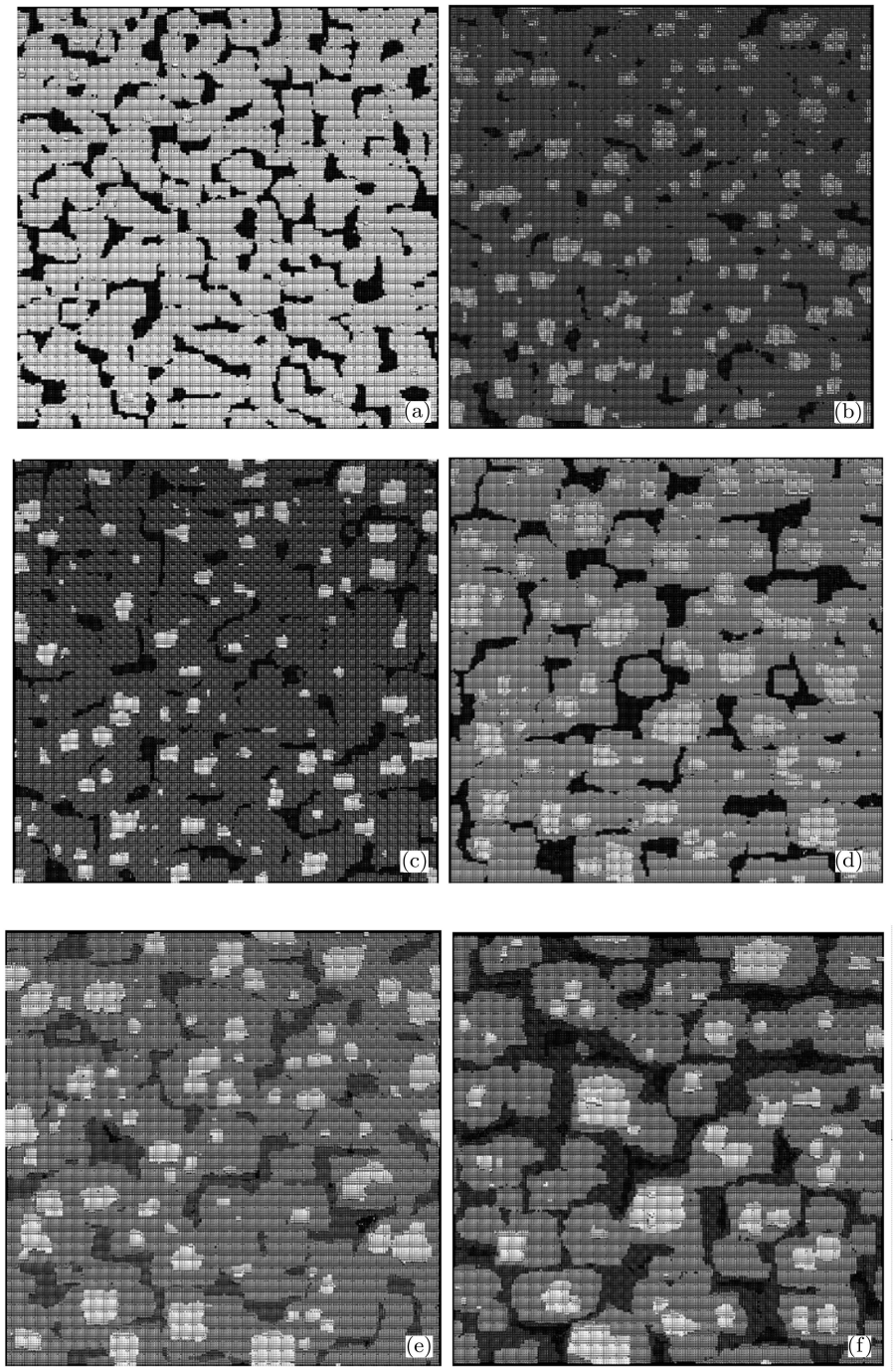


Fig.3. Images of PLD Cu/Pd(100) thin films with different thicknesses: (a) 0.85, (b) 2.1, (c) 3.05, (d) 6.0, (e) 9.0 and (f) 12 ML, deposited at 300 K. The size of the image is 200 × 200 lattice and the scale of grey from white to black represents the top layer to bottom layer, respectively.

The good layer-by-layer growth of the PLD Cu/Pd(100) film is mainly attributed to the instantaneous deposition in the PLD growth as is known in previous publications.[3,6] In fact, although the deposition rate in a pulse is extremely high (10^4 ML/s), there are only 10^{-4} ML atoms deposited during a very short pulse (34 ns). Moreover, there is more sufficient time for the deposited atoms to diffuse between the pulses, yielding an easier growth with layer-by-layer mode. Figure 4 shows the morphologies of TD growth and PLD growth at 0.5 and 5.0 ML, respectively. Obviously, the islands are smaller in the TD growth than in the PLD growth, while the island density is less in the PLD growth than in the TD growth. At low cov-

erages ($\theta = 0.5$ ML), the islands growth under both PLD and TD are two-dimensional, and their roughnesses are almost the same (∼0.5), as shown in Figs.1 and 2. However, at high coverages ($\theta = 5.0$ ML), the growth mode in the TD is typical 3D one, while it remains in a layer-by-layer mode in the PLD growth and the roughness in TD (~ 0.7) is larger than that in PLD (~ 0.55). Of course, the growth modes in the TD and PLD depend on deposition rate dramatically. Higher deposition rate will give rise to rougher growth. On the other hand, it is reasonable that the heterogeneous substrate of Pd reduces the ES barrier of Cu/Pd(100) system, while the ES barrier of Cu/Cu(100) is more than 0.1 eV in value.[47,48] It is evident that there is no difference in ES barrier between the TD and the PLD growths, since there is no evidence that the PLD affects the structures and properties of the substrate as well as the interactions between adatom and substrate. However, how the Pd(100) heterogeneous substrate affects the growth mode has not been available so far.

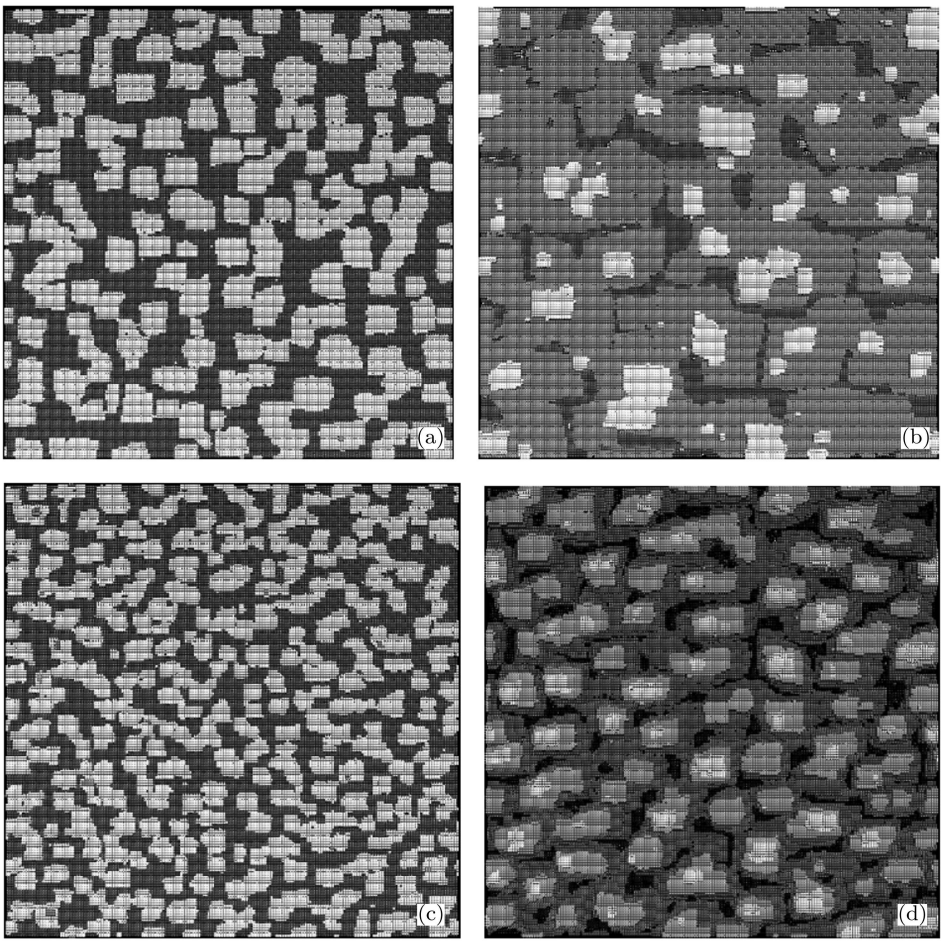


Fig.4. Morphologies for PLD and TD growths at two coverages: 0.5 and 5.0 ML. The images in top row are for PLD growth at room temperature, where the growth condition is the same as that in Fig.3, and the images in bottom row are for TD growth at room temperature where $F = 0.0017$ ML/s.

In order to acquire more detailed information about film growth mode, the layer distribution versus total coverage is calculated as shown in Fig.5. It seems that the second layer growth starts at a coverage of 0.9 ML. At a coverage of 1.0 ML, 95% of the first layer is completed while the remaining 5% appears as the second layer. This two-layer growth mode or perfect layer-by-layer mode remains in a coverage range from 1–6 ML. However, in a thin film thickness range of 6–9 ML, the film growth is in a three-layer form, i. e. the S-K growth mode. Particularly, at 9.0 ML, only 70% of the ninth layer is completed while the remaining 30% appears as the 10th and 11th layers. And above 9 ML, the film grows into one with four or more layers at the same time, which is a perfect 3D growth mode. The film surface becomes more and more rough.

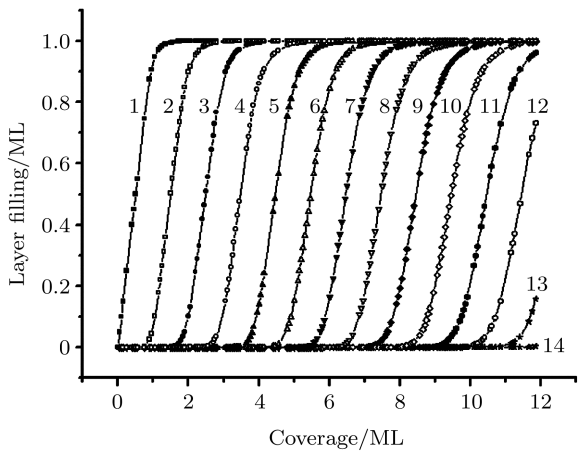


Fig.5. Layer coverage as a function of total coverage of Cu/Pd(100) system at room temperature and $E_{\rm es} = 0.08\,{\rm eV}$. This plot gives the quantitative information about the layer distribution and growth mode. Numbers 1–14 refer to the numeral orders of curves for the first to fourteenth layers.

Both the experimental and the simulation results indicate that the growth mode of Cu/Pd(100) depends dramatically on the coverage. The 2D growth mode at lower coverages has to do with the topmost layer islands which are small and irregularly shaped in the first monolayers. A similar cause has also been considered to be responsible for the observed re-entrant layer-by-layer growth mode in the case of Pt/Pt(111).[50]. As far as the changes of the island size and shape are concerned, they are attributed to the reducing of influence of the substrate as coverage increases.[51] In fact, with increasing coverage, more and more defects will appear on the surface. The completion of this kind of defect will become difficult, i.e. the surface wetting is poor, leading to the conversion from layer-by-layer growth to 3D growth. On the other hand, the surface temperature also plays a significant role in the mobility of adatoms and consequently affects the growth mode of multilayer thin film formation.[48] At relative lower temperatures, the mobility of deposited atoms is slow, resulting in multiple islands formed on the surface and higher values of surface roughness. With increasing temperature, the mobility of adatoms will become so fast that the coalescence effect takes place significantly, yielding the occurrence of layer-by-layer growth mode.

4. Conclusions

In summary, the detailed heteroepitaxial growth of multilayer Cu/Pd(100) by PLD is reproduced by using KMC method, and so are the effects of edge diffusion along the islands, mass transport between interlayers and the instantaneous deposition. The surface roughness and the layer distribution versus total coverage are calculated so as to investigate detailed growth processes during the formation of multilayer thin film. Three kinds of growth modes, i.e. layer-by-layer growth, S-K growth, and 3D growth modes are given at different coverages. It is shown that the layer-by-layer growth mode at the early stage in the growth of Cu/Pd(100) heteroepitaxy by using PLD is mainly attributed to the instantaneous deposition, which is in good agreement with experiments. The ES barrier $E_{\rm es} = 0.08 \pm 0.01\,{\rm eV}$ in Cu/Pd(100) is estimated by comparing the KMC simulation results with the realistic experimental results. The simulation results also show that the growth mode depends on the coverage and substrate temperature dramatically during thin film formation.

Nevertheless, it should be emphasized that the physical conditions of PLD are by far less well defined than those of MBE. The particles deposited may be atoms, clusters, or even droplets.[52] A full theoretical modelling of the kinetic growth process under the PLD experimental conditions is unfeasible yet. Furthermore, although our results provide an estimation of the ES barrier of Cu/Pd(100) heteroepitaxial system, they do not explain the mechanism (e.g. hopping and exchange) for interlayer diffusion. The future work using *ab initio* and molecular dynamics calculations is necessary to clarify the route to understanding the interlayer diffusion.

Acknowledgment

We would like to thank Dr Ling-wang Wang of the Computational Research Division at the Lawrence Berkeley National Lab and Dr Xiangrong Ye of Department of Material Science and Chemical Engineering, University of California at San Diego for helpful discussion.

References

[1] Bozzolo G, Garces J E, Noebe R D, Abel P and Mosca H O 2003 *Prog. Surf. Sci.* **73** 79

[2] Zhang Z Y and Lagally M G 1997 *Science* **276** 377

[3] Jenniches H, Shen J, Mohan C V, Sundar Manoharan S, Barthel J, Ohresser P, Klaua M and Kirschner J 1999 *Phys. Rev.* B **59** 1196

[4] Zhang Z Y, Lu X C, Luo J B, Shao T M, Qing T and Zhang C H 2006 *Chin. Phys.* **15** 2697

[5] Wang Y X, Wen J, Tang Y Q, Guo Z, Tang H G and Wu J X 1998 *Chin. Phys.* **7** 589

[6] Ohresser P, Shen J, Barthel J, Zheng M, Mohan C V, Klaua M and Kirschner J 1999 *Phys. Rev.* B **59** 3696

[7] Lu Y F, Przybylski M, Nyvlt M, Winkelmann A, Yan L, Shi Y, Barthel J and Kirschner J 2006 *Phys. Rev.* B **73** 035429

[8] Chrisey D B and Hueber G K 1994 *Pulsed Laser Deposition of Thin Films* (New York: Wiley)

[9] Lu Y F, Przybylski M, Trushin O, Wang W H, Barthel J, Granato E, Ying S C and Ala-Nissila T 2005 *Phys. Rev. Lett.* **94** 146105

[10] Murray P W, Stensgaard I, Lægsgaard E and Besenbacher F 1995 *Phys. Rev.* B **52** R14404

[11] Bilic A, Shen Y G, King B V and Connor D J O 1998 *Surf. Rev. Lett.* **5** 959

[12] Hahn E, Kampshoff E, Walchli N and Kern K 1995 *Phys. Rev. Lett.* **74** 1803

[13] Kraft T, Marcus P M, Methfessel M and Scheffer M 1993 *Phys. Rev.* B **48** 5886

[14] Ehrlich G and Hudda F G 1966 *J. Chem. Phys.* **44** 1039

[15] Schwoebel R L and Shipsey E J 1966 *J. Appl. Phys.* **37** 3682

[16] Schwoebel R L 1969 *J. Appl. Phys.* **40** 614

[17] Stumpf R and Scheffler M 1994 *Phys. Rev. Lett.* **72** 254

[18] Kodiyalam S, Khor K E and Das Sarma S 1996 *Phys. Rev.* B **53** 9913

[19] Tian Z J and Rahman T S 1993 *Phys. Rev.* B **47** 9751

[20] Jacobsen J, Jacobsen, K W, Stoltze P and Norskov J K 1995 *Phys. Rev. Lett.* **74** 2295

[21] Villarba M and Johnsson H 1994 *Surf. Sci.* **317** 15

[22] Li Y and DePristo A E 1994 *Surf. Sci.* **319** 141

[23] Meyer J A, Vrijmoeth J, van der Vegt H A, Vlieg E and Behm R J 1995 *Phys. Rev.* B **51** 14790

[24] Smilauer P and Harris S 1995 *Phys. Rev.* B **51** 14798

[25] Bromann K, Brune H, Roder H and Kern K 1995 *Phys. Rev. Lett.* **75** 677

[26] Markov I 1996 *Phys Rev.* B **54** 17930

[27] Amar J G and Family F 1995 *Phys. Rev.* B **52** 13801

[28] Mao H B, Jing W P, Yu J G, Wang J Q, Wang L and Dai N 2006 *Acta Phys. Sin.* **55** 5435 (in Chinese)

[29] Liu Z L, Zhang X F, Yao K L, Wei H L and Huang Y M 2004 *Chin. Phys.* **13** 2115

[30] Xie F, Wang X P, Shi Q W and Zhao T X 2003 *Chin. Phys.* **12** 778

[31] Zheng X P, Zhang P F, Liu J, He D Y and Ma J T 2004 *Acta Phys. Sin.* **53** 2687 (in Chinese)

[32] Zhang Q Y, Pan Z Y and Tang J Y 1999 *Chin. Phys.* **8** 296

[33] Zhang Q Y, Ma T C, Pan Z Y and Tang J Y 2000 *Acta Phys. Sin.* **49** 297 (in Chinese)

[34] Tang X, Zhang C and Zhang Q Y 2005 *Acta Phys. Sin.* **54** 5797 (in Chinese)

[35] Clarke S, Wilby M R and Vvedensky D D 1991 *Surf. Sci.* **255** 91

[36] Ogura S, Fukutani K, Matsumoto M, Okano T, Okada M and Kawamura T 2006 *Phys. Rev.* B **73** 125442

[37] Johnson M D, Orme C, Hunt A W, Graff D, Sudijono J L, Sander L M and Orr B G 1994 *Phys. Rev. Lett.* **72** 116

[38] Smilauer P and Vvedensky D D 1995 *Phys. Rev.* B **52** 14263

[39] Siegert M and Plischke M 1996 *Phys. Rev.* E **53** 307

[40] Schroeder M, Smilauer P and Wolf D E 1997 *Phys. Rev.* B **55** 10814

[41] Shitara T, Vvedensky D D, Wilby M R, Zhang J, Neave J H and Joyce B A 1992 *Phys. Rev.* B **46** 6815

[42] Perkins L S and DePristo A E 1994 *Surf. Sci.* **319** 225

[43] Stoltze P 1994 *J. Phys: Condens. Matter.* **6** 9495

[44] Johnson M D, Orme C and Hunt A W 1994 *Phys. Rev. Lett.* **72** 116

[45] Smilauer P, Wilby M R and Vvedensky D D 1993 *Phys. Rev.* B **47** 4119

[46] Elsholz F and Schöll E 2004 *Appl. Phys. Lett.* **84** 4167

[47] Wu F M, Lu H J and Wu Z Q 2006 *Chin. Phys.* **15** 807

[48] Durukanoglu S, Trushin O S and Rahman T S 2006 *Phys. Rev.* B **73** 125426

[49] Kunkel R, Poelsema B, Verheij L K and Comsa G 1990 *Phys. Rev. Lett.* **65** 733

[50] Poulopoulos P, Lindner J, Farle M and Baberschke K 1999 *Surf. Sci.* **437** 277

[51] Shen J, Gai Z and Kirschner J 2004 *Surf. Sci. Rep.* **52** 163