

# Influence of growth temperature on formation of continuous Ag thin film on ZnO surface by ultra-high vacuum deposition

T C Zhang, Z X Mei, Y Guo, Q K Xue and X L Du

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

E-mail: [xldu@aphy.iphy.ac.cn](mailto:xldu@aphy.iphy.ac.cn)

Received 14 October 2008, in final form 15 January 2009

Published 3 March 2009

Online at [stacks.iop.org/JPhysD/42/065303](http://stacks.iop.org/JPhysD/42/065303)

## Abstract

Growth of an Ag film on a ZnO (0001) surface by ultra-high vacuum deposition has been investigated by field emission scanning electron microscopy. It is revealed that the growth temperature has a considerable effect on the formation of a continuous Ag thin film on a ZnO surface. At room temperature or above, the formation of continuous Ag films with small thickness was found to be difficult due to an upstepping mechanism, whereas a continuous Ag film as thin as 30 nm was achieved at 140 K, resulting from the reduced migration length of silver atoms and the increased saturated island density at low temperature. Coalescence between the islands occurred and predominated over upstepping during subsequent deposition, which is favourable for the formation of a continuous Ag film with a smaller thickness.

Recently, numerous studies have been focused on the deposition of metal films on semiconductor substrates, since the interface between them plays a key role in a wide range of applications such as catalysts, microelectronic and photovoltaic devices [1]. Investigations on metal/ZnO systems have also been attracting more and more attention, due to the wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) of ZnO, making it an excellent candidate for short wavelength optoelectronic devices. Metal/ZnO contacts (both Schottky and Ohmic) can be used in ultraviolet (UV) photodetectors [2, 3], which are really important in both commercial and military applications. The metal films, usually applied as conductive electrodes, should be continuous for a good conductivity and be thin enough for a high transmittance.

Silver films have been employed in ZnO Schottky UV photodetectors [3], and a lot of research has been carried out on the growth of Ag films on ZnO [4, 5]. In our work, we find that it is difficult to prepare a continuous Ag film with a thickness of tens of nanometres at room temperature or above. Coalescence of the film usually happens above hundreds of nanometres. The transmission behaviour of such a thicker electrode film is greatly weakened. Therefore, it is necessary

to study the influence of growth temperature on the growth dynamics of Ag films on ZnO.

A two-dimensional (2D) island growth mode is proposed for the deposition of many noble metals [1] on ZnO polar surfaces at room temperature and below. Under a certain coverage, which is usually dozens of monolayers, the metals exist in a feature of separated islands [4]. Beyond the coverage, however, connection of the islands takes place, and a continuous film is formed when it is thick enough. The performance of a photodetector using such a film as electrodes is supposed to depend strongly on the thickness.

In the present study, Ag films with different thicknesses were grown on both ZnO bulk crystals and epitaxial films at different growth temperatures by the ultra-high vacuum deposition method. Recent studies demonstrate much higher p-type doping efficiency in Zn-polar films compared with O-polar ones [6, 7]. Although the origin of p-type conduction in Zn-polar ZnO films has not been quite clear yet, it is a very important surface both for the synthesis of ZnO materials and fabrication of related devices. In our work, the Zn-polar ZnO (0001) surface, both of bulk crystals and epi-films, was hence chosen for Ag deposition of all our samples. The

morphologies were investigated by field emission scanning electron microscopy (FE-SEM), and the influence of growth temperature on the formation of continuous Ag thin films on ZnO (0001) surfaces was revealed. By using a 2D island growth technique at low temperature, a continuous Ag film as thin as 30 nm was achieved at 140 K.

The ZnO (0001) bulk crystals used in this study were prepared by the hydrothermal technique (Tokyo Denpa). The epi-ready Zn-polar surface was used for the deposition of Ag films. The roughness of the surface is less than 0.1 nm. The electron concentration and mobility were  $1 \times 10^{14} \text{ cm}^{-3}$  and  $140 \text{ cm}^2 (\text{Vs})^{-1}$ , respectively, from the van der Pauw measurements at room temperature.

The high-quality ZnO (0001) epitaxial films were grown on nitrated c-plane sapphire substrates by radio-frequency plasma-assisted molecular beam epitaxy (Omni Vac) [8]. The film was 500 nm thick, with an electron concentration of  $1 \times 10^{17} \text{ cm}^{-3}$ , an electron mobility of  $52 \text{ cm}^2 (\text{Vs})^{-1}$  and a surface roughness of 3.5 nm.

The metal-deposition chamber has a heating-cooling sample stage, and the substrate temperature can be varied in a wide range from 700 to 140 K. The base pressure of the chamber was  $1 \times 10^{-8}$  mbar. Ag was evaporated from a commercial K-cell, with an average deposition rate of  $1 \text{ nm min}^{-1}$  on the ZnO (0001) surfaces.

To study the influence of the growth temperature on the growth dynamics of Ag on a bulk ZnO (0001) surface, eight nominal Ag films were prepared at 300 K and 140 K with thicknesses of 7 nm, 14 nm, 25 nm and 35 nm, respectively. Finally, a 60 nm thick Ag film was found continuously at 140 K on the ZnO (0001) surface. To further test the findings, Ag films were grown on ZnO (0001) epitaxial films with a thickness of 30 nm at 140 K, 300 K and 473 K, respectively. For comparison, two more samples were prepared at 300 K with thicknesses of 60 nm and 90 nm, respectively. The surface morphologies of the Ag films were characterized by FE-SEM, and the film thicknesses were confirmed by a surface profiler (Dektak 8, Digital Instruments, Veeco Metrology Group) and atomic force microscopy (AFM, SPA400, SII NanoTechnology Inc.).

The morphologies of the Ag films on the ZnO (0001) bulk substrates deposited at 300 K and 140 K are illustrated in figure 1, respectively. Figures 1(a)–(d) are SEM images of the Ag films deposited at 300 K and (e)–(h) at 140 K with different thicknesses respectively. From a comparison of these figures, it can be seen that Ag tends to form 3D islands on the ZnO (0001) surface at the initial growth stage at both of these temperatures. When the deposition continues, however, the coalescence between the separated islands happens in a smaller thickness for 140 K than for 300 K.

From a thermodynamic point of view, the growth mode lies on a comparison of  $\gamma_{\text{m/ox}}$  with the difference between  $\gamma_{\text{ox}}$  and  $\gamma_{\text{m}}$ , where  $\gamma_{\text{m/ox}}$  is metal/oxide interfacial free energy,  $\gamma_{\text{ox}}$  the surface free energy of the oxide and  $\gamma_{\text{m}}$  that of the metal. If

$$\gamma_{\text{m/ox}} > \gamma_{\text{ox}} - \gamma_{\text{m}}, \quad (1)$$

the metal has a tendency to form 3D islands to minimize the surface energy. According to Campbell, mid-transition metals

such as silver prefer this growth mode on oxide surfaces [1], which is consistent with our observations.

Statistics of island densities for 7, 14 and 25 nm thick Ag films are shown in table 1. Every datum was obtained from the average of 5 maps in a scan area of  $10 \times 10 \mu\text{m}^2$ . From these data, three obvious features can be concluded: (1) the island density decreases with the thickness of the film increasing at both of these temperatures; (2) at the initial growth stage, the island density is higher for the films grown at 140 K (low temperature) than those at 300 K (room temperature); (3) the island density decreases more rapidly at low temperature.

The above observations can be well explained by a coalescence process which happens after the island density is saturated at the initial growth stage. According to Campbell [1], a saturated nuclei density  $N_0$  is reached when the deposited atoms run into existing nuclei before making new nuclei with other migrating atoms. After that, the nuclei grow larger and higher until they connect to each other with the island density decreasing. The growth of epitaxial islands on a crystalline substrate can be described by the following theoretical equation:

$$\ln \left( \frac{N}{N_0} \right) = -AN_0^{\frac{1}{3}}h^{\frac{2}{3}}, \quad (2)$$

where  $N$  is the nucleation density,  $N_0$  the island density at the very beginning of the deposition,  $h$  the average thickness,  $A$  a constant which depends on the shape of the islands [9]. This indicates that the island density decreases with the growth of the film because of the islands' coalescence.

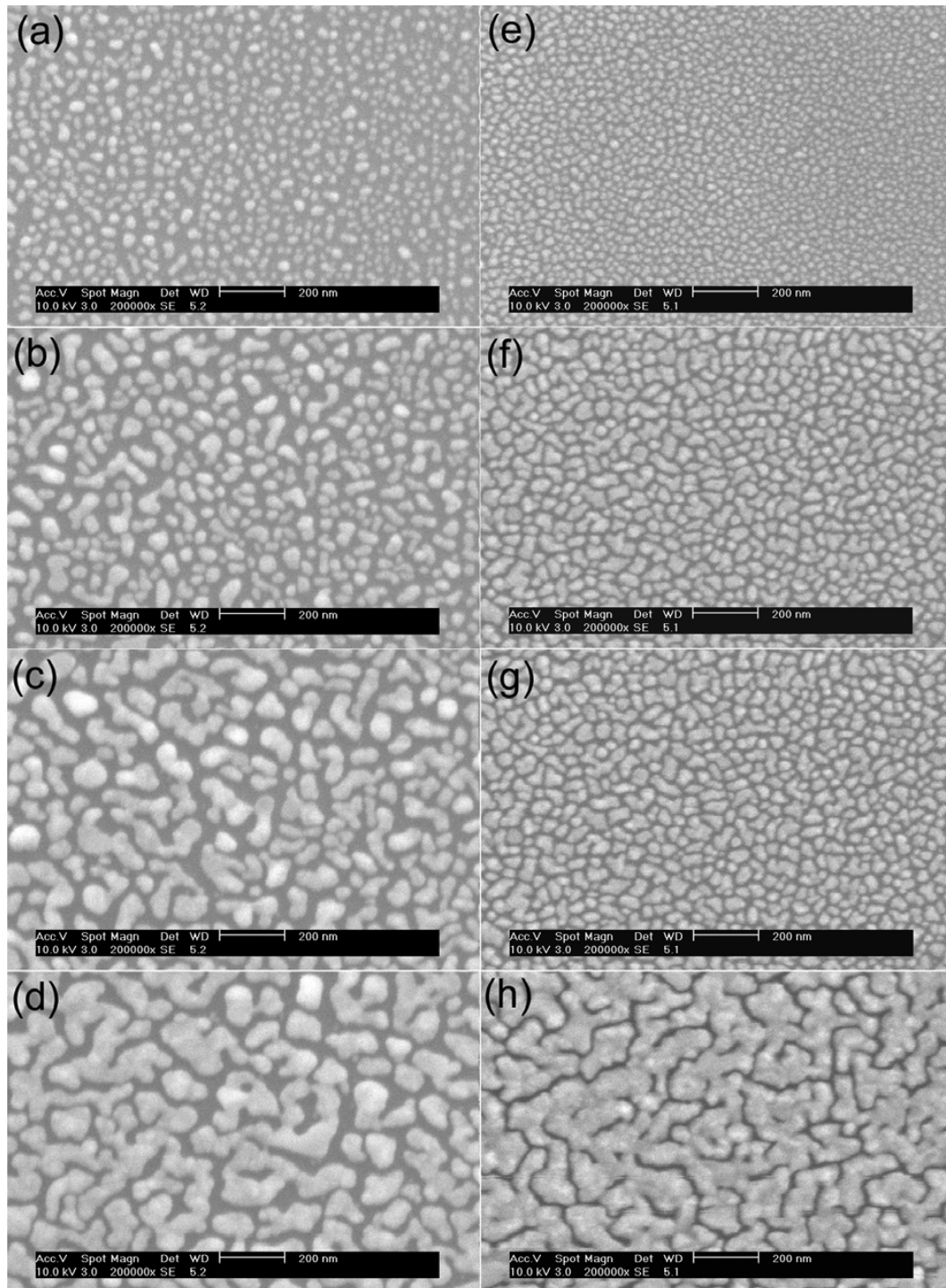
Since  $N_0$  relates to the nuclei process, it depends on the atom's diffusion ability on a surface, the diffusion coefficient, which can be expressed as

$$D = D_0 \exp \left( -\frac{E_{\text{diff}}}{k_{\text{B}}T} \right), \quad (3)$$

where  $D_0$  is the prefactor which can be considered as a constant when  $T$  is high enough [10], and  $E_{\text{diff}}$  is the diffusion activation energy. It is known that the saturated island density  $N_0$  decreases with increasing diffusion coefficient  $D$  [1]. Hence  $N_0$  decreases with increasing growth temperature.

It is reasonable that the migration length of silver atoms on the ZnO (0001) surface will be reduced at low temperature, and that will help the formation of a high nucleation density. In our work,  $N_0$  was calculated to be  $2.6 \times 10^{11} \text{ cm}^{-2}$  and  $1.0 \times 10^{12} \text{ cm}^{-2}$  at 300 K and 140 K, respectively, which agrees very well with the above analysis. It was also observed that the density of the nuclei decreased with increasing surface temperature for the case of Pd and Au deposition on MgO (001) [11–13]. That is why the island density is higher for the Ag films grown at 140 K than those at 300 K at the initial growth stage.

The feature (3) demonstrates the difference in coalescing speeds between the two deposition temperatures, which depends mainly on the islands' lateral growth. The migrating atoms reaching the edges of the islands can either stick there or upstep onto the island terraces, similarly to the case of Cu on ZnO surfaces [14]. The thermal energy is found important



**Figure 1.** SEM images of Ag films deposited on bulk ZnO (0001) surfaces at (a)–(d) 300 K and (e)–(h) 140 K. The average thicknesses are (a) (e) 7 nm, (b) (f) 14 nm, (c) (g) 25 nm and (d) (h) 35 nm.

in the upstepping movement, i.e. higher islands with larger spacings tend to form at higher temperatures, while islands with wandering edges locate much closer to each other at lower temperatures, as illustrated in figure 1. The rapid spreading of the islands accelerated the coalescing with the islands' density decreasing, which promoted the formation of continuous Ag films.

The Ag film shown in figure 2 was grown on the ZnO (0001) bulk substrate at 140 K, with a thickness of 60 nm. The

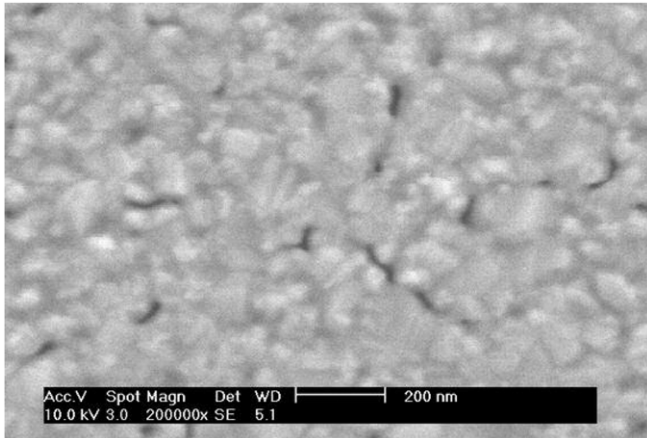
gap between the islands was almost filled, and a continuous Ag film was obtained at this thickness. It should be noted, however, that the Ag film grown at 300 K could not coalesce into a continuous structure until 120 nm thick.

Growth of Ag on the ZnO (0001) epitaxial film at various temperatures was also investigated in order to test our above findings. Figure 3 shows the morphologies of the Ag films with a thickness of 30 nm deposited at 140 K, 300 K and 473 K, respectively. It can be seen that a continuous film is easily



**Table 1.** Island densities for six Ag films with different thicknesses deposited on ZnO (000 1) bulk substrates at 300 and 140 K.

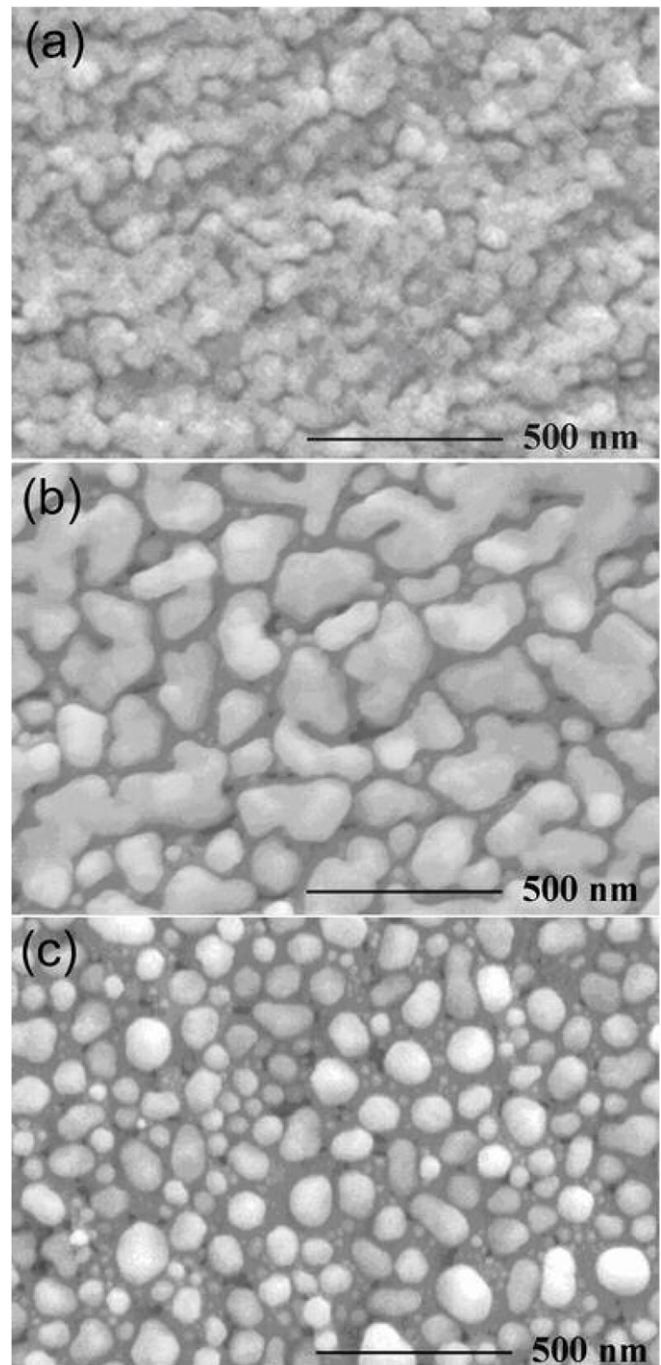
Film thickness (nm)	Island density $N$ ( $\times 10^{10}$ cm $^{-2}$ )	
	At 300 K	At 140 K
7	6.25	12.5
14	2.60	3.75
25	1.06	0.75

**Figure 2.** SEM image of continuous Ag film deposited on bulk ZnO (000 1) surface at 140 K. The average thickness is 60 nm.

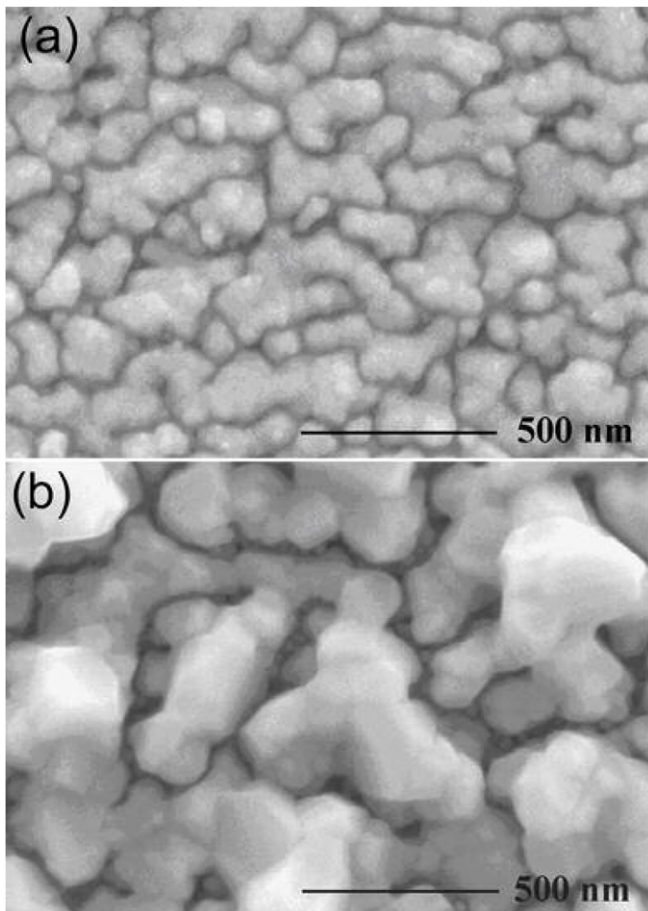
formed at 140 K (figure 3(a)). It should be noticed that this thickness is much smaller than that on the ZnO (000 1) bulk (60 nm). The much higher defect density in the ZnO (000 1) epitaxial film was supposed to play a key role in providing additional nucleating centres and accelerating the coalescing process [15]. The surface of this Ag film is not as smooth as that on bulk ZnO (000 1), which is caused by the rougher surface morphology of the epitaxial ZnO (000 1) film.

The effect of the growth temperature on the competition between coalescence and upstepping of islands is further confirmed by the Ag films grown at 300 and 473 K. Figure 3(b) shows the Ag film deposited at 300 K, where the islands' coalescence is apparent but not adequate. Due to the higher thermal energy of 300 K compared with 140 K, the lateral connection of the islands is slowed down and suppressed by the upstepping mechanism at this temperature. The upstepping movement becomes dominating when the temperature increases to 473 K, as shown in figure 3(c). The edges of the islands are much smoother and the vacant spaces between them are much broader. The islands grow more rapidly in the vertical direction than in the horizontal one at this high temperature. Low nucleation density and dominant upstepping growth of some transition metals on ZnO surfaces at high substrate temperatures have been reported [16, 17]. Our results agree well with the traditional theory about metal film or particles deposition on oxide surfaces [1] and the experimental observation of Cu on ZnO [14]. The influence of the growth temperature on the formation of continuous films was hence established in our case of the Ag deposition on the ZnO (000 1) surface.

The competition between coalescence and the upstepping mechanism at room temperature was further demonstrated in

**Figure 3.** SEM images of Ag films deposited on ZnO (000 1) epitaxial films with a thickness of 30 nm at (a) 140 K, (b) 300 K and (c) 473 K.

the deposition of the Ag films with thicknesses of 60 and 90 nm on the ZnO (000 1) epitaxial films (figure 4). From figure 4(a), the island size and the spatial distribution look nearly identical to those in figure 3(b), while the island height is slightly larger. When the thickness of the Ag film reaches 90 nm (figure 4(b)), the islands are still isolated although the size and height increase at the same time, which indicates that the arriving atoms prefer the upstepping sites to the laterals at this temperature. It should be noted that the continuous film will be finally realized with a thickness of over 100 nm, which is not expected in many practical device applications.



**Figure 4.** SEM images of Ag films deposited on ZnO (0001) epitaxial films at 300 K with a thickness of (a) 60 nm and (b) 90 nm.

In conclusion, the effect of growth temperature on the growth behaviour of Ag film on the Zn-polar (0001) surface of ZnO bulk crystals and single-crystalline films by ultra-high vacuum deposition was investigated. It was found that the formation of a continuous Ag thin film on the ZnO (0001) surface was greatly influenced by the growth temperature. At a lower temperature, the reduced migration length of silver atoms leads to a higher saturated island density, and the enhanced coalescence speed of Ag islands

results in the formation of a continuous film with a smaller thickness. On the other hand, the thickness is much bigger at a higher temperature, which is mainly caused by the prevailing upstepping movement against lateral growth.

### Acknowledgments

This work is supported by the National Science Foundation (Grant Nos 50532090, 60606023, 60621091, 10804126), Ministry of Science and Technology (Grant Nos 2007CB936203, 2009CB929400) of China and Chinese Academy of Sciences.

### References

- [1] Campbell C T 1997 *Surf. Sci. Rep.* **27** 1
- [2] Yang W, Vispute R D, Choopun S, Sharma R P, Venkatesan T and Shen H 2001 *Appl. Phys. Lett.* **78** 2787
- [3] Liang S, Sheng H, Liu Y, Huo Z, Lu Y and Shen H 2001 *J. Cryst. Growth* **225** 110
- [4] Duriau E, Agouram S, Morhain C, Seldrum T, Sporcken R and Dumont J 2006 *Appl. Surf. Sci.* **253** 549
- [5] Sahu D R, Lin S-Y and Huang J-L 2007 *Sol. Energy Mater. Sol. Cells* **91** 851
- [6] Guo X-L, Choi J-H, Tabata H and Kawai T 2001 *Japan. J. Appl. Phys. Part 2* **40** L177
- [7] Look D C, Reynolds D C, Litton C W, Jones R J, Eason D B and Cantwell G 2002 *Appl. Phys. Lett.* **81** 1830
- [8] Mei Z X, Du X L, Wang Y, Ying M J, Zeng Z Q, Zheng H, Jia J F, Xue Q K and Zhang Z 2005 *Appl. Phys. Lett.* **86** 112111
- [9] Vincent R 1971 *Proc. R. Soc. Lond. A* **321** 53
- [10] LingTi Kong and Lewis L J 2008 *Phys. Rev. B* **77** 165422
- [11] Henry C R, Meunier M and Morel S 1993 *J. Cryst. Growth* **129** 416
- [12] Henry C R, Chapon C, Duriez C and Giorgio S 1991 *Surf. Sci.* **253** 177
- [13] Kubo M, Miura R, Yamauchi R, Vetrivel R and Miyamoto A 1995 *Appl. Surf. Sci.* **89** 131
- [14] Ernst K H, Ludviksson A, Zhang R, Yoshihara J and Campbell C T 1993 *Phys. Rev. B* **47** 13782
- [15] Heim K R, Coyle S T, Hembree G G, Venables J A and Scheinfein M R 1996 *J. Appl. Phys.* **80** 1161
- [16] Dulub O, Boatner L A and Diebold U 2002 *Surf. Sci.* **504** 271
- [17] Sahu D R and Huang J-L 2006 *Mater. Sci. Eng. B* **130** 295