Science in China Ser. G Physics, Mechanics & Astronomy 2004 Vol.47 No.5 612—620

Role of gallium wetting layer in high-quality ZnO growth on sapphire (0001) substrates

ZENG Zhaoquan[1,3], WANG Yong[2], DU Xiaolong[1], MEI Zengxia[1], KONG Xianghe[3], JIA Jinfeng[1], XUE Qikun[1] & ZHANG Ze[2,4]

1. State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China;
2. Laboratory of Electron Microscopy, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China;
3. College of Physics and Engineering, Qufu Normal University, Qufu 273165, China;
4. Beijing University of Technology, Beijing 100022, China

Correspondence should be addressed to Zeng Zhaoquan (email: zqzeng@aphy.iphy.ac.cn)

Received April 27, 2004

Abstract A Ga wetting layer was used to modify the surface structure of sapphire (0001) substrate to prepare high-quality ZnO film by radio frequency plasma-assisted molecule beam epitaxy. We found that this Ga layer plays a crucial role in eliminating 30° rotation domains, controlling polarity and decreasing defect density in ZnO epilayers, as demonstrated by *in situ* reflection high energy electron diffraction, *ex situ* high resolution X-ray diffraction and high resolution cross-sectional transmission electron microscopy. Zn-polar film of ZnO was determined by convergent beam electron diffraction. A Ga bilayer model is proposed to understand the effects of the Ga wetting layer on high-quality ZnO growth.

Keywords: Ga wetting layer, sapphire, polarity, defect density, zinc oxide, rf-MBE, RHEED, HRXRD, TEM, CBED.

DOI: 10.1360/03yw0271

ZnO is a wide direct bandgap (E_g=3.37 eV at room temperature) II-VI compound semiconductor of wurtzite structure (a = 3.249 Å, c = 5.207 Å). Compared to GaN and ZnS, ZnO has a larger exciton binding energy, ~60 meV (cf. ~25 meV for GaN and ~40 meV for ZnS), which is advantageous to realizing low-threshold excitonic lasers. Since optically pumped UV lasing of ZnO at room temperature was reported in 1997[1], much attention has been paid to the crystal quality improvement and p-type conduction realization in ZnO thin films. Similar to the case of GaN epitaxy, sapphire (0001) has been extensively used as the substrate for ZnO epitaxial growth due to its high crystal quality and low cost. However, the formation of rotation domains in ZnO epilayers[2], which results from the large lattice mismatch between sapphire (0001) (a = 4.754 Å, c = 12.99 Å) and ZnO[3], degrades the crystal quality of epilayers. Moreover, inversion domains[4],

which are domains with an opposite polarity to the matrix, were often found in wurtzite ZnO grown on sapphire (0001). Polarity of wurtzite-type semiconductors is a key factor that affects the electrical and optical properties, as well as the doping behaviors of these materials[5–8]. It is very essential to develop some special techniques to eliminate rotation domains and inversion domains so as to achieve high-quality ZnO film.

The surface structure of sapphire (0001) substrate just before ZnO film growth plays an important role in their epitaxial orientationship, and is responsible for the formation of rotation domains and inversion domains[9,10]. Corundum α-Al_2O_3 has rhombohedral symmetry[11], in which oxygen atoms form a hcp-type structure (ABAB...), and aluminum atoms take a fcc-type stacking (abcabc...) sequence[12]. The hexagonal structure of oxygen atom sub-lattice has a 30° in-plane rotation along *c* axis with respect to that of aluminum atom lattice. Three possible surface termination layers, i.e. an Al monolayer, an Al bilayer and an O layer, have been proposed for the *c*-plane of α-Al_2O_3[13]. The Al monolayer-terminated sapphire surface has been confirmed to be the most stable surface by low-energy electron diffraction[14] and X-ray scattering studies[15]. The coexistence of rotation domains and inversion domains was observed in ZnO epilayers directly grown on these three surface structures[2, 9, 10]. In general, ZnO is epitaxially grown on the oxygen sub-lattice with a lattice mismatch of 18.4%, which forms the main domains with an in-plane epitaxial relationship of $\langle 11\bar{2}0 \rangle ZnO // \langle 10\bar{1}0 \rangle Al_2O_3$. However, epitaxy of ZnO on aluminium sub-lattice also occurs despite the large lattice mismatch (31.8%), which introduces the 30° rotation domains with the epitaxial orientationship of $\langle 11\bar{2}0 \rangle ZnO // \langle 11\bar{2}0 \rangle Al_2O_3$. In that case, two kinds of domains with opposite polarities will be generated, resulting in the quality degradation of ZnO films[4]. Du et al. has performed systematic studies on the origins of these rotation domain and a new kind of rotation domain was observed[9,10]. In their work, an effective preconditioning method was adopted to modify the sapphire (0001) surface, i.e. depositing a thin Ga wetting layer after the oxygen plasma pretreatment. In this way, they obtained high-quality ZnO thin films, but the exact role of Ga wetting layer in the improvement of ZnO film crystal quality is still an open question. In this paper, by using *in situ* reflection high energy electron diffraction (RHEED) and *ex situ* high resolution X-ray diffraction (HRXRD), transmission electron microscopy (TEM) and convergent beam electron diffraction (CBED), we have investigated the effects of Ga wetting layer on rotation domain elimination, dislocation density reduction and polarity control of ZnO epilayers.

1 Experiment

The radio frequency plasma-assisted molecule beam epitaxy (rf-MBE) system we used was modified from a conventional MBE system (MBE-IV, Shen Yang Ke Yi). Zinc and gallium were supplied by evaporating elemental Zn (6N) and elemental Ga (6N) from commercial Knudsen cells, respectively. Active oxygen radicals were produced by the rf-plasma system (HD25R, Oxford Applied Research). The base pressure of the growth chamber was $\sim 1.2 \times 10^{-7}$ Pa.

After degreased in trichloroethylene and acetone, the sapphire substrates were chemically etched in a hot solution of H_2SO_4 : H_3PO_4=3 : 1 at 140℃ for 30 min to remove the surface contamination and the damaged surface layer by mechanical polishing. After introduced into the growth chamber, the substrates were thermally cleaned at 750℃ for 30 min and then exposed to the oxygen radicals for 30 min at 400℃ with an rf power of 300 W and oxygen pressure of 1.0×10^{-2} Pa. After the oxygen plasma pretreatment, the plasma source was switched off and the chamber was rapidly pumped down to 3×10^{-6} Pa. A thin Ga layer was deposited on the above prepared surface at 820℃ for 22 s with a deposition rate of 0.2 Å/s. A two-step growth method for ZnO was then employed, i.e. high-temperature epilayer growth at 650℃ after low-temperature buffer layer growth at 400℃. A high-resolution X-ray diffractometer (Philips) was used to characterize the crystallinity of the ZnO epilayers and investigate the in-plane epitaxial relationship between ZnO and sapphire (0001). The role of Ga wetting layer in eliminating rotation domains and inversion domains and reducing dislocation densities was studied by TEM (Philips CM12 TEM).

2 Results and discussion

2.1 Effects of the Ga wetting layer on growth of ZnO films with single domain

Fig. 1 shows the evolution of RHEED patterns during growth. Before Ga predeposition, the sapphire substrate shows a sharp streaky pattern (fig. 1(a)), which indicates a clean and flat surface after thermal cleaning and oxygen plasma pretreatment. The subsequent Ga deposition did not cause any obvious change in the RHEED pattern. This suggests that no new structure is formed, which is in agreement with the high-resolution TEM observation. At the initial stage of ZnO buffer layer growth, the RHEED pattern of the sapphire substrate disappears, and a streaky pattern appears with 30° rotation against that of the sapphire substrate (fig. 1(b)). Further growth of ZnO leads to a diffuse spotty pattern, as shown in fig. 1(b). These observations suggest that the initial growth of ZnO on sapphire (0001) follows typical Stranski-Krastanov mode[3].

For ZnO growth, the first ZnO layer will act as a wetting layer by the formation of strong bonds between O atoms and underlying Ga atoms on the sapphire surface. This ZnO layer overlaps the oxygen sub-lattice of the sapphire substrate, which corresponds to a 30° rotation against the sapphire lattice. The initial two dimensional (2D) nucleation of ZnO films is most likely related to the existence of this wetting layer. The lattice mismatch between ZnO epilayer and sapphire substrate is greatly reduced from 31.8% to 18.4% by the ZnO superposition on the oxygen sub-lattice. However, a lattice mismatch of 18.4% is still significant enough to introduce a lot of strains, which will be partly relaxed via forming three dimensional (3D) islands as growth is continued. Therefore the spotty RHEED patterns should be expected, corresponding to a growth mode transition from 2D nucleation to 3D nucleation. The RHEED patterns of the as-grown ZnO epilayer are very sharp (fig. 1(c)), which indicates a smooth surface of ZnO film. Mean-

while, no rotation domains can be observed, and the ZnO film is of single domain. In addition, the epitaxial orientation relationship of $\langle 11\bar{2}0\rangle$ZnO//$\langle 10\bar{1}0\rangle Al_2O_3$can be derived from the change of azimuthal directions in RHEED patterns.

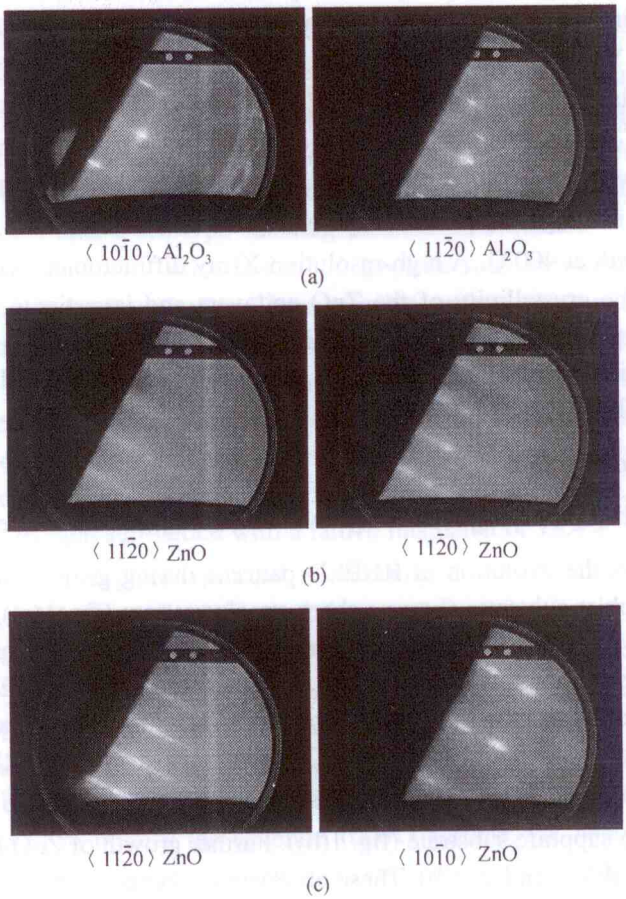

Fig. 1. RHEED patterns of (a) sapphire substrate before Ga deposition; (b) ZnO buffer layer grown for 2 and 7 min respectively; (c) ZnO epilayer grown for 3 h.

The HRXRD ϕ scans of asymmetric ZnO$\{10\bar{1}2\}$ and $Al_2O_3\{11\bar{2}3\}$ were performed to determine the in-plane orientation (fig. 2). Within the ϕ scan range from 0° to 360°, only six diffraction peaks are observed in fig. 2(a), which suggests that no rotation domains exist in the ZnO epilayer. The epitaxial orientation relationship obtained from RHEED patterns can be confirmed by comparing the positions of the six peaks of ZnO$\{10\bar{1}2\}$ with those of $Al_2O_3\{11\bar{2}3\}$. These results demonstrate that the predeposition of the Ga wetting layer on sapphire (0001) surface plays an important role in the elimination of rotation domains.

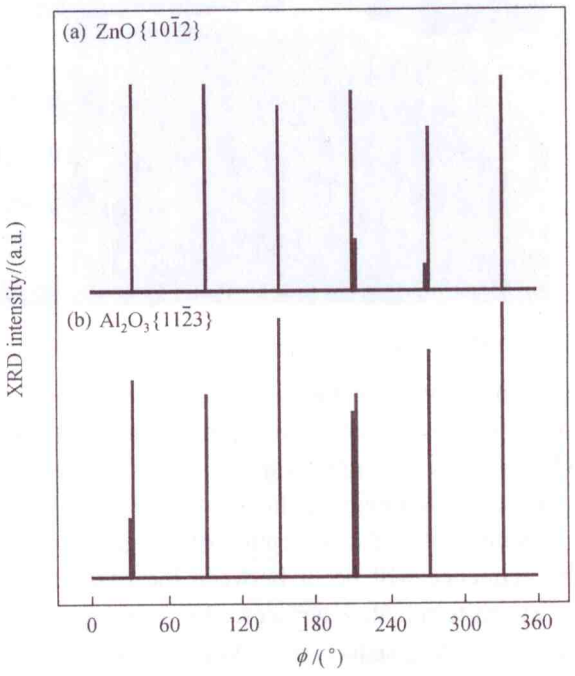

Fig. 2. HRXRD ϕ-scans of ZnO film and sapphire substrate. (a) ZnO {10$\bar{1}$2} ; (b) Al_2O_3 {11$\bar{2}$3} .

2.2 Role of Ga wetting layer in eliminating inversion domains

The TEM experiments were carried out to determine the polarity of ZnO film. Fig. 3(a) shows a cross-sectional TEM image of the as-grown ZnO film under weak-beam diffraction conditions at 100 kV with g=[0002]. Along the growth direction, the defect structure varies in three different regions, which will be discussed in sec. 2.3. It should be noted that no inversion domains were found in the ZnO epilayer in our various TEM characterizations. To determine the polarity of the sample, we selected some dislocation-free regions and performed a CBED experiment using a FEG-CM200, which is operated at 200 kV with a 50 μm condensed aperture and a 960 nm camera length. The CBED pattern was taken near 〈1$\bar{1}$00〉 ZnO zone axis, with a small angle away from the axis toward 〈11$\bar{2}$0〉 ZnO direction. In this case, the electron diffraction from (0002) Zn and (000$\bar{2}$) O faces could be easily identified by the fringes in the CBED disk, as shown in fig. 3(b), which is similar to the pattern of GaN[16]. Since the (0002) Zn face reflects the electron beam much more strongly than the (000$\bar{2}$) O face, the centre fringes at (0002) and (000$\bar{2}$) disks should appear bright and dark, respectively. And the fringes in (0000) disk are symmetrical because the electrons are exactly parallel to the (0001) plane. Thus, the tokens in the CBED pattern indicate that the ZnO film has a [0001] polarity, i.e. Zn polarity.

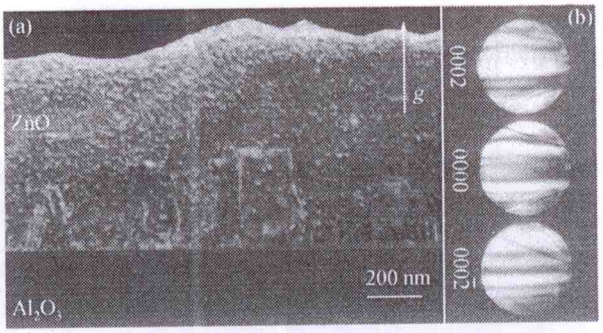

Fig. 3. A cross-sectional TEM image of the ZnO film in a dark field with g=[0002] (a) and its CBED pattern (b).

It is well known that inversion domains tend to be formed in the ZnO films directly grown on sapphire substrates. Inversion domains' boundaries are often observed in the cross-sectional TEM images of ZnO samples[4]. An oxygen-layer-terminated sapphire surface formed by exposure to oxygen radicals is not stable, and some part of the surface is terminated by aluminum after the desorption of oxygen atoms. In this case, two kinds of atomic bonding sequence will occur between the first ZnO layer and the sapphire surface. On the oxygen-terminated terraces, the stacking sequence will be O (substrate)-Zn-O-, while a bonding sequence of Al (substrate)-O-Zn- will be formed on the aluminium termination layers, which result in O-polar and Zn-polar domains, respectively. On the Ga-wetting layer modified sapphire (0001) surface, however, a bonding sequence of Ga(Al)-O-Zn- should be energetically favourable, and the formation of O-polar inversion domains is greatly suppressed. Thus, ZnO film with sole Zn polarity will be yielded, as demonstrated in our CBED study.

2.3 Role of Ga wetting layer in reducing defect density

Three different defect structures were found in three regions along the growth direction (fig. 3(a)). A lot of defects exist in the interface. In the middle layers, however, the interaction of threading dislocations results in the formation of dislocation loops, which is obviously different from the case of the ZnO film directly grown on sapphire substrate, where dislocations formed at the interface tend to penetrate the whole epilayer up to the surface. The strong interaction between these threading dislocations in the intermediate region makes the dislocation density in the upper region of the epilayer drop greatly to about 8.0×10^8 cm^{-2}, and the upper ZnO epilayer has good crystallinity and orientational uniformity along the c axis. The dislocation structures in ZnO film are also confirmed by HRXRD ω scan result of ZnO(0002). The full width at half maximum (FWHM) of the (0002) diffraction peak is as small as 115 arcsec (fig. 4). However, this sharp peak is accompanied with a long tail, which is corresponding to the high defect density in the region near ZnO/sapphire interface[2].

A cross-sectional high-resolution TEM study at 200 kV with the spatial resolution of 0.25 nm was carried out to investigate the defects and heterostructure of the interface

layer. The micrograph taken along the $\langle 11\bar{2}0 \rangle$ZnO zone axis (fig. 5(a)) clearly shows that the ZnO/Ga/sapphire interface is atomically sharp with no amorphous layer or layer with new structure. This indicates that monoclinic Ga_2O_3 by oxidization of the Ga wetting layer did not form at the interface[17], which is consistent with the fact that no obvious change occurs in the RHEED patterns of sapphire after Ga predeposition.

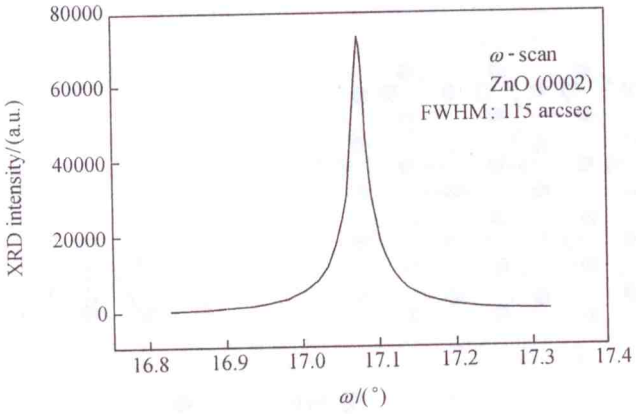

Fig. 4. HRXRD ω-scan of ZnO(0002). The FWHM is as small as 115 arcsec.

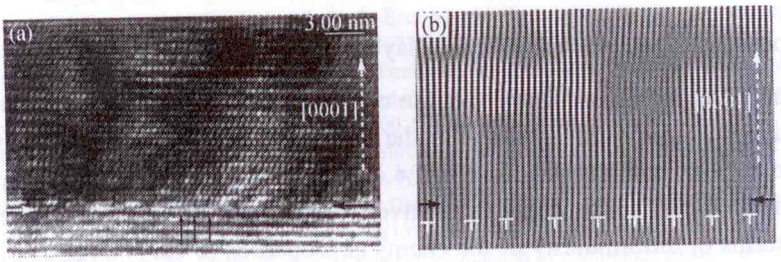

Fig. 5. (a) High resolution cross-sectional TEM image of ZnO film near the ZnO/Ga/Al_2O_3 interface (shown by horizontal arrows). The terminated planes are corresponding to the misfit dislocations which are marked by vertical arrows; (b) Fourier-filtered image of fig. 5(a). For every five or six ZnO $\{1\bar{1}00\}$ planes there is a redundant sapphire $\{1\bar{2}10\}$ plane corresponding to the misfit dislocations marked in the interface.

Furthermore, the space lattice image of ZnO is clearer than that of sapphire, which is attributed to the 30° in-plane rotation of ZnO lattice with respect to the sapphire substrate. It should be mentioned that the micrograph was taken in $\langle 11\bar{2}0 \rangle$ZnO zone axis, equivalent to $\langle 10\bar{1}0 \rangle$ sapphire zone axis. The 30° rotation results in a mismatch of 18.4% between sapphire and ZnO. The large lattice mismatch is accommodated by domain matching of lattice constants, where seven $\{1\bar{2}10\}$ planes of sapphire match five or six $\{1\bar{1}00\}$ planes of ZnO film, as demonstrated in the Fourier-filtered image (fig. 5(b)). Therefore, the Ga wetting layer did not reduce the lattice mismatch between ZnO and sapphire. It can be seen from the Fourier-filtered image that most of the dislocations

are formed in the initial stage of ZnO growth and confined in the interface. The Ga wetting layer increases the mixed dislocations density in the interface layer by some unknown mechanism and enhances the interaction of the threading dislocations in the middle layers. In addition, it effectively suppresses the formation of rotation domains and inversion domains by modifying the sapphire surface and thus reduces the defects density in ZnO epilayer.

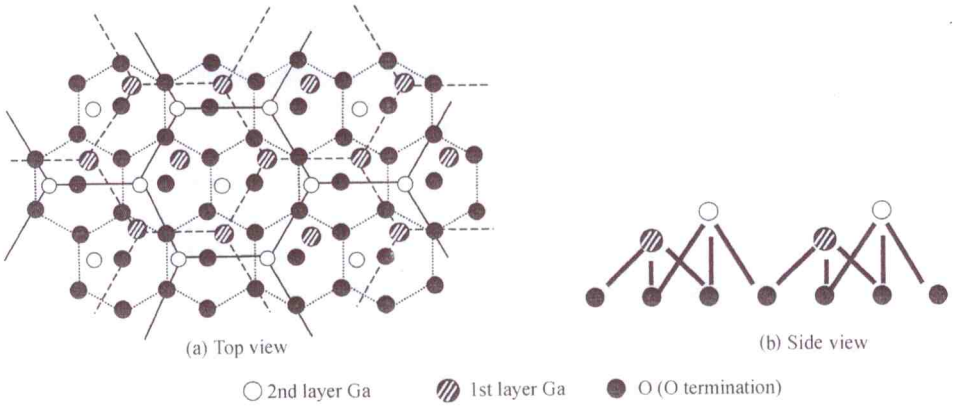

Fig. 6. Schematic illustration of Ga bilayer deposited on an O-teminated sapphire (0001) surface. (a) Top view; (b) side view.

2.4 Proposed mechanism of Ga wetting layer on improved crystal quality

In our experiments, we found that the coverage of Ga is very critical for growth of high quality ZnO films. ZnO film with the best quality and Zn polarity was obtained only when the Ga layer has a thickness of 4.4 Å. ZnO films tend to be deteriorated, such as the formation of rotation domains or inversion domains for higher or lower Ga coverage. In terms of the similarity of the chemical properties of Ga and Al, and the similar atomic and ionic radii of Ga (1.81 Å and 0.62 Å) and Al (1.82 Å and 0.53 Å), two monolayers of Ga should be formed, as shown in fig. 6. We propose a Ga bilayer model, in which Ga atoms form an ideal Ga wetting layer of two monolayers thick by bonding to oxygen atoms on substrate surface and maintaining a corundum structure, equivalent to an Al bilayer termination surface[13]. According to this model, oxygen atoms in the first layer of ZnO film will keep the hcp-type structure of the oxygen sub-lattice in sapphire and form an interface stacking sequence: -O-Ga-Ga-O-Zn-, corresponding to the atomic stacking sequence for Zn polarity. This is consistent with the RHEED and TEM observations. When the Ga coverage is lower, the bilayer cannot cover the whole substrate surface and some one-monolayer Ga-terminated regions will be formed. ZnO film grown on these regions will give rise to the lattice structure of Al atoms (31.8% lattice mismatch) and a 30° rotation with respect to that on the Ga bilayer terminated regions, as seen from fig. 6. On the other hand, when the Ga coverage is too high, Ga atoms above the Ga bilayer cannot be confined in the interface layer and will diffuse into the ZnO epilayer due to the weak bonding. The diffused Ga atoms may be incorporated into

the ZnO layer and become a donor, which influences the electrical properties and crystallinity of ZnO films, as confirmed by our experiments.

3 Summary

High-quality ZnO thin films have been grown on sapphire (0001) substrates modified by using a Ga wetting layer, and its influence on the crystallinity and polarity of ZnO film has been studied in detail. On the Ga-bilayer covered sapphire surface, rotation domains and inversion domains were effectively suppressed, and Zn-polar ZnO films with best quality were obtained. A model has been proposed to understand the results.

Acknowledgements The authors would like to thank Prof. Zhou Junming for the technical assistance. This work was supported by the National Natural Science Foundation of China (Grant Nos. 60376004, 10174089, and 60021403), and the Nation Key Basic Research and Development Programme of China (Grant No. 2002CB613502).

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