Polarity control of ZnO films on (0001) Al2O3 by Cr-compound intermediate layers

J. S. Park, S. K. Hong, T. Minegishi, S. H. Park, I. H. Im et al.

Citation: Appl. Phys. Lett. 90, 201907 (2007); doi: 10.1063/1.2740190
View online: http://dx.doi.org/10.1063/1.2740190
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v90/i20
Published by the American Institute of Physics.
Polarity control of ZnO films on (0001) Al$_2$O$_3$ by Cr-compound intermediate layers

J. S. Park$^{a)}$
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

S. K. Hong
Department of Nano Information Systems Engineering, Chungnam National University, Daejeon 305-764, Korea

T. Minegishi, S. H. Park, I. H. Im, T. Hanada, M. W. Cho,$^{b)}$ and T. Yao$^{b)}$
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

J. W. Lee and J. Y. Lee
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

(Received 2 February 2007; accepted 24 April 2007; published online 15 May 2007)

This letter presents a reliable and very easy method for selective growth of polarity controlled ZnO films on (0001) Al$_2$O$_3$ substrates by plasma-assisted molecular-beam epitaxy. Cr-compound intermediate layers are used to control the crystal polarity of ZnO films on (0001) Al$_2$O$_3$. ZnO films grown on rocksalt structure CrN/(0001) Al$_2$O$_3$ shows Zn polarity, while those grown on rhombohedral Cr$_2$O$_3$/(0001) Al$_2$O$_3$ shows O polarity. Possible interface atomic arrangements for both heterostructures are proposed. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2740190]

ZnO is an attractive material for applications to ultraviolet optoelectronic devices owing to its wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. ZnO crystallizes in wurtzite structure and naturally has crystal polarity along the c axis: Zn polar and O polar. Chemical, optical, and electrical properties of ZnO are dependent on crystal polarity. It has been reported that the efficiency for impurity doping in GaN depends on crystal polarity. Crystal polarity is one of the important factors for designing electronic and optoelectronic devices. To date, only a few methods have been reported on the control of crystal polarity of ZnO films on c sapphire. Selective growth of Zn- and O-polar ZnO layers were achieved on c sapphire by using thickness-controlled MgO buffer. Ultrathin AlN buffer layers, which were formed by nitridation of the surface of c sapphire, were used to control the crystal polarity of ZnO layers grown on c sapphire. We mention, however, that special precaution is needed to prepare the MgO and AlN buffers, which play a crucial role in the selective growth of Zn-polar and O-polar ZnO layers on c sapphire.

This letter will report on an easy and reliable method for selective growth of polarity-controlled ZnO films on (0001) Al$_2$O$_3$ substrates by plasma-assisted molecular-beam epitaxy. Cr-compound intermediate layers are used to control the crystal polarity of ZnO films on (0001) Al$_2$O$_3$. ZnO films grown on rocksalt structure CrN/(0001) Al$_2$O$_3$ shows Zn polarity, while those grown on rhombohedral Cr$_2$O$_3$/(0001) Al$_2$O$_3$ shows O polarity. Possible interface atomic arrangements for both heterostructures will be proposed.

---

$^a$Author to whom correspondence should be addressed; electronic mail: jspark@imr.tohoku.ac.jp
$^b$Also at: Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan.
is no additional oxide interfacial layer between the ZnO and CrN, which means that the oxidation of the CrN layer was protected by the Zn preexposure before the growth of the ZnO.\(^{12}\) From the TEM study, we have determined the epitaxial relationship between the ZnO, CrN, and Al\(_2\)O\(_3\) as ZnO(0001)\textbackslash{}CrN(111)\textbackslash{}Al\(_2\)O\(_3\)(0001) and ZnO[2\textendash{}1\textendash{}10]\textbackslash{}CrN[0\textendash{}1\textendash{}1]\textbackslash{}Al\(_2\)O\(_3\)[10\textendash{}10].

Figure 2 shows the cross-sectional HRTEM micrograph for a ZnO film grown on an oxidized CrN/Al\(_2\)O\(_3\) substrate. We can clearly see two intermediate layers between the ZnO and Al\(_2\)O\(_3\). The DDPs for the ZnO, Al\(_2\)O\(_3\), and two intermediate layers are shown in the inset of Fig. 2. The lower intermediate layer is determined to be CrN based on the DDP analysis with the same procedures mentioned in Fig. 1. The DDP from the upper intermediate layer is indexed and determined to be a diffraction pattern for rhombohedral structure Cr\(_2\)O\(_3\) with the 0001 plane parallel to the interface is only (0002). In case of the XRD \(\theta\)-\(2\theta\) scan of ZnO (10\textendash{}11) planes, six peaks regularly spaced by 60° were observed, which indicates that there are no rotational domains.

Let us discuss the crystal polarity of the two kinds of ZnO films shown in Figs. 1 and 2. The polarity of ZnO films was determined by investigating differences in wet etching and growth rate. The difference in etching rate for opposite polar faces has been explained in terms of surface bonding model for A\(_{\text{II}}\)-B\(_{\text{VI}}\).\(^{14}\) The surface Zn layer has a positive charge, while the layer of surface O atoms has a negative charge due to the electron transfer from Zn to O atoms.\(^{15}\) The dangling electrons on O-polar surfaces account for a high etching rate, owing to their susceptibility to reaction with electron-seeking agents, than those on Zn-polar surfaces.\(^{15}\) Hence, both wurtzite-structure III-nitrides and ZnO (Refs. 19 and 20) show different etching rates for surfaces with different crystal polarities, which implies that the polarity determination based on a chemical etching rate is highly reliable. Chemical wet etching rates of ZnO films grown on CrN and Cr\(_2\)O\(_3\)/CrN layers were determined to be 10 and 95 nm/min, respectively; which reveals about ten times higher etching rate for the ZnO film grown on a Cr\(_2\)O\(_3\)/CrN layer. Such remarkable difference in wet etching rate clearly indicates that ZnO films grown on a CrN has Zn polarity, while the one grown on a Cr\(_2\)O\(_3\)/CrN has O polarity. Figures 3(a) and 3(b) show that the surface morphology of ZnO films grown on CrN layer is only slightly changed after chemical etching and that the rms value is only changed from 32.4 to 33.2 nm by chemical etching. To the contrary, the surface of ZnO films grown on Cr\(_2\)O\(_3\)/CrN become rough by chemical etching, as shown in Figs. 3(c) and 3(d). The rms value measures 16.9 and 52.8 nm before and after etching, respectively. All these observed surface features on our samples agree well with the etching characteristics of different polar ZnO films.\(^{15,19,20}\) Therefore, we conclude that ZnO films grown on CrN are Zn polar, while ZnO films on Cr\(_2\)O\(_3\)/CrN are O polar.

It has been reported that the growth rate of Zn-polar ZnO is considerably higher than that of O-polar films.\(^{19,21}\) The higher growth rate for Zn-polar ZnO films can be understood...
Figure 4. (Color online) Schematics of the atomic arrangements of ZnO layers on CrN layer (a) and on Cr2O3 layer (b), which result in Zn-polar and O-polar ZnO, respectively.

in terms of the difference in the sticking coefficient of Zn atoms onto growing surfaces, since the growth of ZnO films is mostly limited by the sticking of Zn atoms rather than that of O atoms under O-rich growth conditions. Each oxygen atom on a Zn-polar surface has three dangling bonds, while each O atom has only one dangling bond on an O-polar surface. Hence, the sticking coefficient of Zn atoms onto an O-terminated surface of Zn-polar ZnO is larger than that onto an O-polar ZnO, which results in a higher growth rate for Zn-polar ZnO films than that for O-polar ZnO films. In our typical growth rate of ZnO films grown on CrN was 7.5 nm/min, while those grown on Cr2O3/CrN showed a growth rate of 4.9 nm/min under the same growth conditions. The growth rate of ZnO films grown on CrN layer is 1.5 times higher than that of ZnO films grown on Cr2O3/CrN layer. Hence, we can conclude that ZnO films grown on CrN are Zn polar, while those grown on Cr2O3/CrN are O polar. This conclusion is consistent with the etching studies described above.

Figures 4a and 4b show schematics of the atomic arrangements of ZnO on CrN and Cr2O3, respectively. The CrN surface is mostly N terminated because the CrN growth was conducted under N-rich growth conditions. In the initial growth of ZnO on CrN, we have employed Zn preexposure to prevent oxidation of the CrN, as mentioned before. Therefore, we expect N–Zn bondings at the interface. Since the topmost N atoms in rocksalt CrN have three dangling bonds, each Zn atom bonded with N atoms has only one dangling bond along the growth direction. O atoms bonding to Zn atoms have three dangling bonds. As a result, ZnO films grown on CrN layer shows Zn polarity, as shown in Fig. 4a. When Cr2O3 is formed by the exposure of oxygen plasma, the topmost surface is likely to be an O-terminated surface based on the reported surface phase diagram. Zn atoms at the interface will occupy octahedral sites bonding to three underlying oxygen atoms in the oxygen layer of Cr2O3 and will simultaneously occupy tetrahedral sites of ZnO as in the case of AlN formation on O-terminated (0001) Al2O3 by nitridation. Therefore, every oxygen atom at the surface has one dangling bond along the c direction, which results in O-polar ZnO layers.

Finally, in order to demonstrate the crucial role of Cr2O3 intermediate layer in determining the polarity of ZnO grown on Al2O3 structure, we have checked the polarity of a ZnO film grown on Cr2O3 without underlying CrN layer. ZnO films grown on the Cr2O3 showed the same growth rate as that of the ZnO film in Fig. 2, which indicates that O-polar ZnO films grow on Cr2O3 layer. Therefore, we can conclude that the key factors for the selective growth of Zn- and O-polar ZnO films on Al2O3 are the use of intermediate layers of CrN with cubic O sublattice and Cr2O3 with hexagonal O sublattice, respectively.

In summary, we have controlled the polarity of ZnO films grown on (0001) Al2O3 by using Cr-compound intermediate layers. Single crystalline ZnO films were grown on (111) CrN and (0001) Cr2O3 layers by PAMBE. Phases and crystal structures of the intermediate layers and epitaxial relationships were investigated by HRTEM. A very low chemical etching rate and a higher growth rate were observed for ZnO films grown on CrN layer, while a high chemical etching rate and a lower growth rate were observed for those grown on Cr2O3 layer. Based on these observations, the polarity of ZnO films grown on rocksalt structure CrN is determined to be Zn polar, while O-polar ZnO films are grown on rhombohedral Cr2O3 layer. Possible interface atomic arrangements for both heterostructures are proposed.

The CNU portion was supported by Korea Research Foundation Grant funded by Korea Government (MOEHRD, Basic Research Promotion Fund) (KRF-2005-205-D00078).

13The RHEED pattern became steady on impinging O plasma onto a CrN surface, while the reciprocal spacing was varied from the change of the 40° for that to Cr2O3.