Polarity determination of ZnO thin films by electron holography

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The polarity of the ZnO film grown on sapphire using an ultrathin Ga wetting layer has been investigated by electron holography. Spontaneous polarization of the ZnO film leads to localized charges in the surface, which change the potential distribution in the vacuum side of the film. The potential distribution depends on the nature of the bounded charges and change as a function of the distance from the film surface. By studying the dependence of the potential change on the distance from the film surface, the ZnO film with very thin Ga wetting layer is determined to have the [0001] polarity. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1669060]

III–V and II–VI compound semiconductor thin films with either wurtzite or zinc-blende structure have attracted great attention in terms of their technological importance in fabrication of high-brightness blue light-emitting diodes and laser diodes.[1,2] In these materials, the polarity in a noncentrosymmetric structure results from the stacking sequence of the (0001) atomic planes in wurtzite-type ZnO and GaN, or the (111) planes in zinc-blende-type GaAs.[2] The polarity is closely related to the film quality such as surface morphology and electronic properties,[2,3] it is important to determine polarity of such a thin film. Many methods, such as energy-dispersive x-ray spectroscopy,[4] coaxial impact-collision ion scattering spectroscopy,[5] convergent beam electron diffraction,[6] high-resolution transmission electron microscopy (HRTEM),[7] and electron energy loss spectroscopy[2] have been developed for the polarity determination.

The polarity of GaN or ZnO may lead to the spontaneous polarization.[8] Recently, the spontaneous polarization and piezoelectric effect have been used to study the polarity of the GaN film.[9] The charges induced by the polarization in the film surface will influence the potential in the vacuum near the film. The potential distribution around the charges depends on the sign of bounded charges and can be used to determine the polarity of the film. As electron holography (EH) can precisely detect the electrical potential distribution in both vacuum and film, it has been successfully used to study the polarity.[10] Recently, ultrathin Ga layer was used to obtain high-quality ZnO film on sapphire (0001) substrate, a dramatic defect reduction was achieved. No inversed domains were found.[11,12] In this letter, we apply EH to determine the polarity of ZnO film grown on (0001) sapphire using Ga wetting layer.

The sample for this study was grown by radio frequency plasma-assisted molecular beam epitaxy (MBE-IV, ShengYangKeYI). A Ga layer was used to modify the sapphire surface. The detailed deposition procedure has been published elsewhere.[11] The cross-section specimen for EH observation was prepared by the conventional method including cutting, gluing, mechanical polishing, and dimpling procedures followed by the Ar^+ ion-beam milling to perforation. A Philips CM200 TEM equipped with a field emission gun and a Gatan image filtering system was operated at 200 kV to carry out the EH experiment. Off-axis holograms formed by applying a positive bias of 90 V on the electrostatic biprism installed at the selective aperture were collected using a Gatan 794 multiscan charge coupled device camera. The holograms with a typical size of 1024×1024 pixels were processed using DIGITALMICROGRAPH program including HOLOWORKS package. The aperture size used for the reconstruction was optimally 1/3 of the carrier frequency.[13] To remove the 2π phase jumps, the phase images were unwrapped using the algorithms developed by Kahl.[14]

ZnO has the same wurtzite structure as GaN.[3] Thus, we define the polarity of ZnO following the conventional notation used for GaN.[15] The [0001]-axis points from the Zn atom to the nearest-neighbor O atom (cation to anion) along the crystallographic *c* axis, and from the O face to the Zn face HB. The orientation of spontaneous polarization is defined by convention such that the positive direction is along the crystallographic [0001] axis. As the sign of the spontaneous polarization is negative,[8] the orientation always points from Zn face to O face (the $[000-1]$ direction). The sign of the charges at the surface of ZnO film due to the polarization is related to the orientation of the polarization and, therefore, to the polarity of the crystal, as shown in Fig. 1(a). For the cross-section specimen of the ZnO film, we denote the outer side of the specimen to the surface of the ZnO film.

The bounded charges at the outer side of the ZnO specimen will inevitably influence the potential distribution in its vicinity. The electron wave function is sensitive to the electric field resulting from the bounded charges and will be disturbed by this potential when passing through the vicinal vacuum. EH supplies direct retrieval of the electron wave function and thus can be used to detect the potential distri-

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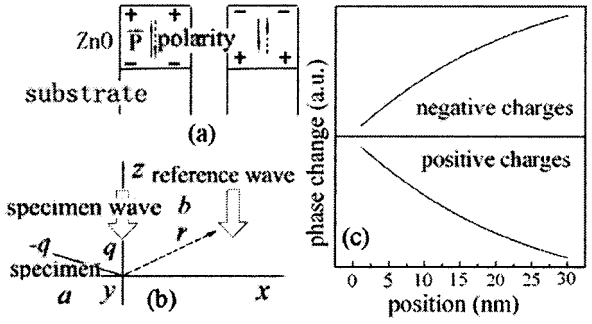

FIG. 1. (a) The schematic diagram of the relation of the spontaneous polarization and the polarity of ZnO film, (b) the schematic model for the discussion of the electric potential distribution in the vacuum region due to the charged edge, (c) the simulated phase change in the vacuum region of the specimen with positive or negative charges.

bution in the vacuum near the charged ZnO film. Without a magnetic field, the phase shift of the object wave with respect to a reference (in vacuum) wave is given by

$$\Delta\Phi(x,y)=C\int V(x,y,z)dz, \tag{1}$$

where V is the potential distribution along the path of the incident electrons passing through the specimen, C $(=2\pi(E+E_0)/\lambda E(E+2E_0))$ is a constant, λ is the electron wavelength and E, E_0 are the kinetic and rest mass energy of the electrons, respectively.[13] To simplify the discussion, we consider the line charges along y direction, one at the outer side, and the other at the substrate side of the film, and the distance between two lines is a, as shown in Fig. 1(b). The length of the line is l. Thus, the electric potential distribution in the vacuum region is approximately given by

$$V(r)=\int_{-l/2}^{l/2}\frac{\rho}{4\pi\varepsilon_0}\left(\frac{1}{\sqrt{x^2+(y-y_1)^2+z^2}}-\frac{1}{\sqrt{(x+a)^2+(y-y_1)^2+z^2}}\right)dy_1. \tag{2}$$

According to Eq. (1), the phase change can be calculated to be

$$\Delta\Phi(x,y)=\frac{\rho C}{4\pi\varepsilon_0}\left\{\left[\left(\frac{l}{2}-y\right)\ln\frac{(x+a)^2+\left(\frac{l}{2}-y\right)^2}{x^2+\left(\frac{l}{2}-y\right)^2}+\left(\frac{l}{2}+y\right)\ln\frac{(x+a)^2+\left(\frac{l}{2}+y\right)^2}{x^2+\left(\frac{l}{2}+y\right)^2}\right]+2(x+a)\times\left[\mathrm{tg}^{-1}\left(\frac{\frac{l}{2}-y}{x+a}\right)+\mathrm{tg}^{-1}\left(\frac{\frac{l}{2}+y}{x+a}\right)\right]-2x\left[\mathrm{tg}^{-1}\left(\frac{\frac{l}{2}-y}{x}\right)+\mathrm{tg}^{-1}\left(\frac{\frac{l}{2}+y}{x}\right)\right]\right\}. \tag{3}$$

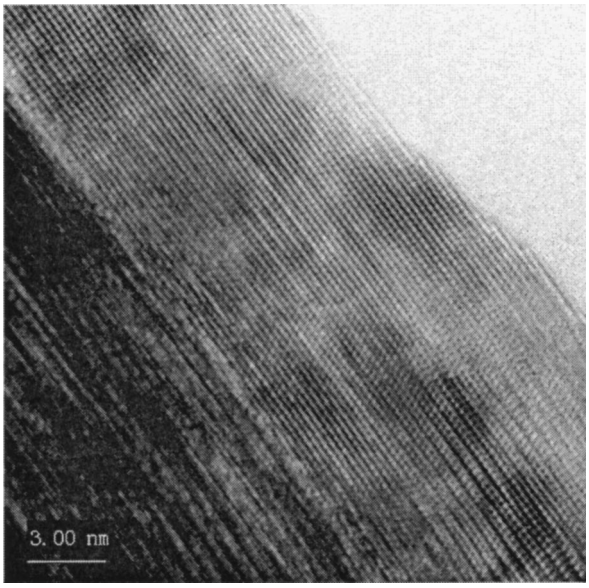

FIG. 2. The HREM image of ZnO film.

However, due to the leakage field in the vacuum due to the bounded charges in the outer side, the phase of reference wave was also disturbed. Thus the phase change detected by EH should be $\Delta\varphi_1-\Delta\varphi_0=\Delta\Phi(x,y)-\Delta\Phi(x+b,y)$ where $\Delta\varphi_1$ is the phase change in the specimen wave, and $\Delta\varphi_0$ is the extra phase change in the reference wave as it is disturbed by the leakage field. b is the distance between the "reference" and "object" waves. Assuming $l=50$ nm, $a=20$ nm, $y=0$ nm and $b=30$ nm, Fig. 1(c) shows the calculated phase distribution in the vacuum close to the specimen edge with the different charges. It can be clearly seen that the phase profiles in the vacuum near the edge of specimen have opposite distance dependence for the different charges. Thus, the sign of the bounded charges in the outer side of ZnO specimen can be determined unambiguously based on the measured phase profile in the vacuum near the edge of the specimen. It must be noted that the specimen has wedge shape. If the specimen thickness can be determined accurately, the quantitative analysis on the charge distribution is also possible.

Usually, there is an amorphous layer on the surface of the ion-milled specimen. The amorphous layer will influence the bounded charges in the edge of the specimen. For deprivation of the amorphous layer, the specimen was ion-milled by Ar^+ with low voltage for several minutes just before TEM observation. The HREM image (Fig. 2) of the ZnO film shows clearly the crystalline structure without amorphous layer at the rim.

Figure 3(a) shows the electron hologram of the ZnO film. A reference hologram was also collected without the presence of the specimen in the view field for the purpose of elimination of distortions due to incoherent illumination and spherical aberration during reconstruction of the hologram. Figure 3(b) is the phase image reconstructed from Fig. 3(a) together with the reference hologram. One-dimensional profile was extracted by line scans perpendicular to the ZnO film and is shown in Fig. 3(c). This profile was averaged over 50 line scans along the direction normal to the scanning direction for improvement of the signal-to-noise ratio.

It is known from the previous discussion that the char-

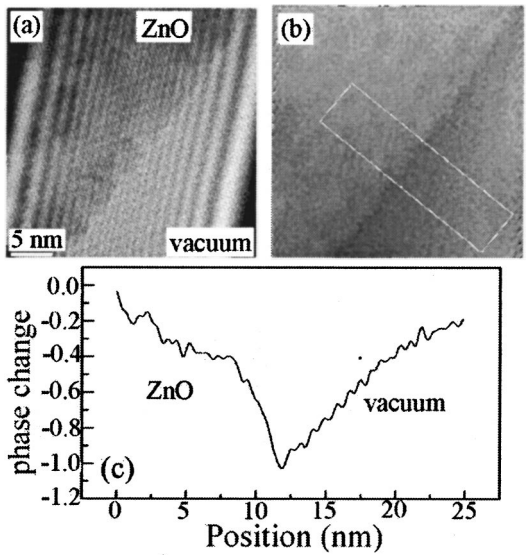

FIG. 3. (a) The hologram of ZnO film, (b) the phase image reconstructed from (a) using a reference hologram taken without presence of the specimen, and (c) the averaged one-dimensional phase change profile obtained from the boxed area in (b).

acteristic of the measured phase profile coincides with the negatively charged edge. The accumulation of electrons in the specimen during TEM observation should not be significant, as in the case of MgO.[16] Thus, the negative charges bounded in the outside rim of ZnO could be attributed to the spontaneous polarization in the ZnO film, which pointed to the substrate. Due to the antiparallel relationship between the spontaneous polarization and the polarity of the ZnO film, the polarity for the present case is [0001], i.e., the film has the [0001] orientation.

A thin metallic Ga layer was deposited before the ZnO, which leads to a Ga-terminated surface. On the Ga-terminated surface, a deposition sequence of Ga–O–Zn should be energetically favorable. This atomic sequence could lead to the [0001] polarity of the ZnO film. It has been reported in literature that the quality of the ZnO film will be better for the [0001] polarity,[3] therefore, a thin metallic layer such as Ga should be recommended for use as a buffer layer on sapphire substrate in order to control the atomic sequences of the ZnO expilayer during the deposition and improve its properties.[11,12]

In summary, we have applied electron holography to determine the polarity of the ZnO film with an ultrathin Ga wetting layer. The bounded negative charges induced by the spontaneous polarization in the film surface have been determined by direct measurement of the phase shift in the vicinal vacuum, and we find that the spontaneous polarization points to the substrate and the polarity of the ZnO film is [0001]. The [0001] polarity results from the thin Ga wetting layer, which changes the interface bonding configuration and inverts the atomic sequences from the Zn–O–Zn–to the O–Zn–O–.

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