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Polarity of wurtzite crystals by photoelectron diffraction

I. Bartoš, O. Romanyuk*

Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 00 Prague 6, Czech Republic

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ABSTRACT

Photoelectron diffraction is proposed to determine nondestructively the polarity of wurtzite crystals with polar surfaces (*c*-plane). Small segments of polar plots of photoemission from anion core levels in the (1 0 $\bar{1}$ 0) azimuthal plane are qualitatively different for two polarities around the polar angle 20°. The magnitude of the ratio of electron photoemission intensities at two polar angles I_{20}/I_{23} can be utilized as a simple criterion determining the crystal polarity.

1. Introduction

Wurtzite semiconductors exhibit a strong charge transfer between strongly electronegative anions (N, O) and their electropositive metal counterparts (In, Ga, Al). The charge redistributions give rise to a macroscopic polarization and strong internal electric fields. This polarization is oriented along the *c*-axis of these crystals and it strongly affects the material and device properties of these semiconductors.

The two polarizations are referred to as cation-face or anion-face polarity depending on whether the cation atoms or anion atoms of the cation–anion bilayers forming the crystal are facing toward the crystal surface. In cation-face crystals, the crystallographic *c*-axis is conventionally defined to point away from the surface.

The potential benefits for improved device performance of wurtzite semiconductors raise a question about fast and nondestructive ways of determining their polarity. Among them, approaches utilizing photoelectron diffraction appear promising. The fact that the angular distributions of photoemitted electron intensities differ for the two crystal terminations has been used to determine the polarity of GaN [1], ZnO [2] and InN [3,4] by X-ray photoelectron diffraction (XPD). These XPD analyses were complicated and time consuming, sometimes requiring synchrotron radiation excitation, however. Photoelectron diffraction patterns can be investigated in detail in order to find directions in which photoemission intensities show significant differences for the two polarities. Specific experimental geometries can help to avoid rather demanding mapping of the whole hemisphere of XPD intensities. Here, we suggest polar plots of intensities in a small range of angles excited by a standard laboratory MgKα excitation as sufficient for determining the polarity of wurtzite crystals with polar surfaces.

The wurtzite structure is formed by two interpenetrating close packed hexagonal sublattices, each consisting of one type of atom and displaced with respect to each other along the *c*-axis by the amount *u* (*u* = 3/8*c* in an ideal structure, *c* is a unit cell size along the [0 0 0 1] direction). In the binary compound semiconductors each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. Viewed along the *c*-axis, the atomic planes of cations and anions alternate regularly. These planes are denoted as *c*-planes and here crystals with these polar surfaces will be investigated. The ideal wurtzite is formed by bilayers stacked along the *c*-axis with a smaller intralayer separation ($\sqrt{6}/3$ of the anion–cation bond length corresponding to the bonds to the three bottom tetraeder corners) than that between two neighboring bilayers (the full bond length corresponding to the bond to the tetraeder top corner) [5]. The different electronegativity of the atoms forming the wurtzite bilayer gives rise to the electric polarity of the crystal. Two possible surface terminations of wurtzite crystals, by the surface cation or anion atomic plane, are determined by the bulk polarity orientation due to the intra-bilayer firmness. Different surface termination gives rise to pronounced differences of wurtzite polar surface properties like adsorption, electric properties or interface formation. Though unit cell dimensions of wurtzites *a* and *c* vary by more than 1 Å, the ratio *c*/*a* (ideal value 1.633) and the internal parameter *u*, which determine the angular variations within the structure

* Corresponding author. Tel.: +420 220 318 495.
E-mail address: romanyuk@fzu.cz (O. Romanyuk).

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Table 1
Crystal lattice constants a and c (Å) [16], inner parameter u, cation to anion atomic size ratio R_c/R_a [9] and the total electron scattering cross-section ratio σ_c/σ_a [17]. The total scattering cross-sections for energies corresponding to the emissions from anion 1s core levels are given. Cation scatterers dominate in all wurtzite crystals except BeO.

	a	c	c/a	u	R_c/R_a	σ_c/σ_a
Ideal	–	–	1.633	0.375	–	–
AlN	3.111	4.978	1.600	0.382	1.92	2.26
GaN	3.190	5.189	1.627	0.377	2.00	2.91
InN	3.533	5.693	1.611	0.378	2.38	4.37
SiC	3.079	5.053	1.641	0.376	1.57	2.53
ZnO	3.253	5.213	1.603	0.382	2.23	2.51
BeO	2.698	4.380	1.623	0.378	1.75	0.83

and are important for our analysis, differ very little (under 2%, see Table 1) for wurtzite carbide, oxides and nitrides. These differences can be neglected in our considerations.

It was realized a long time ago that the wurtzite crystal polarity can be determined nondestructively from the angular distributions of electron intensities photoemitted from the polar (0 0 0 1) surface plane of GaN [1] and InN [3] where hemispherically scanned X-ray photoelectron diffraction has been employed. Recently, it has been shown that instead of measuring full angular distribution, the polar plots of intensities are sufficient [4,6]. The azimuth of the polar plot then remains to be selected. There are two higher symmetry planes perpendicular to the surface: the nonpolar $(1\,1\,\bar{2}\,0)$ a-plane and the nonpolar $(1\,0\,\bar{1}\,0)$ m-plane. The $(1\,0\,\bar{1}\,0)$ plane with vertical pairs of interlayer bonded cation and anion atoms (Fig. 1) contains a smaller number of atoms, displays a simpler structure and polar plots in this azimuth appeared to differ for the two polarities much more than for the $(1\,1\,\bar{2}\,0)$ plane [4]. Therefore, the $(1\,0\,\bar{1}\,0)$ azimuthal plane is to be preferred for the analysis.

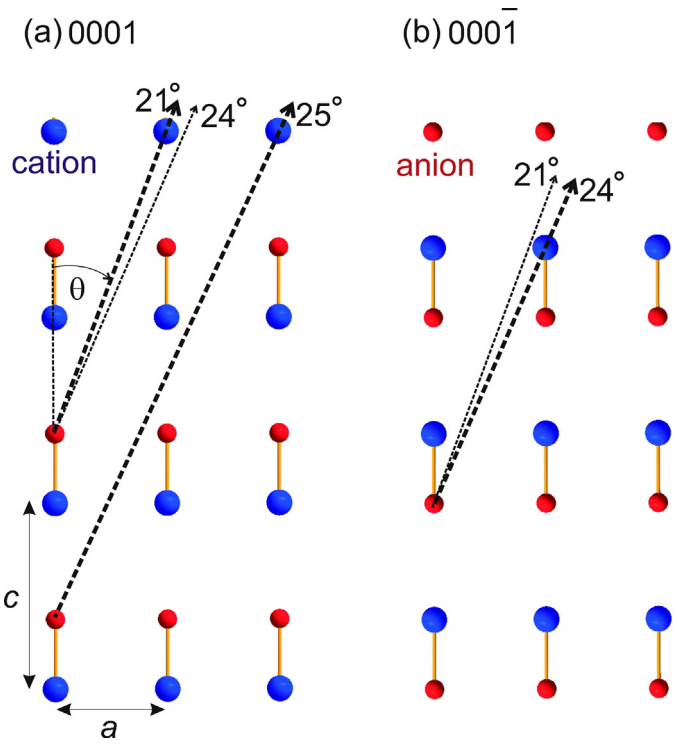

Fig. 1. Side view of the $(1\,0\,\bar{1}\,0)$ atomic planes of the ideal (a) cation-terminated and (b) anion-terminated wurtzite surface. Directions connecting anion emitters (smaller red circles) with cation scatterers (larger blue circles) in the surface region are given for anion–cation pairs oriented within the range 20–25° (polar angles are measured from the surface normal). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

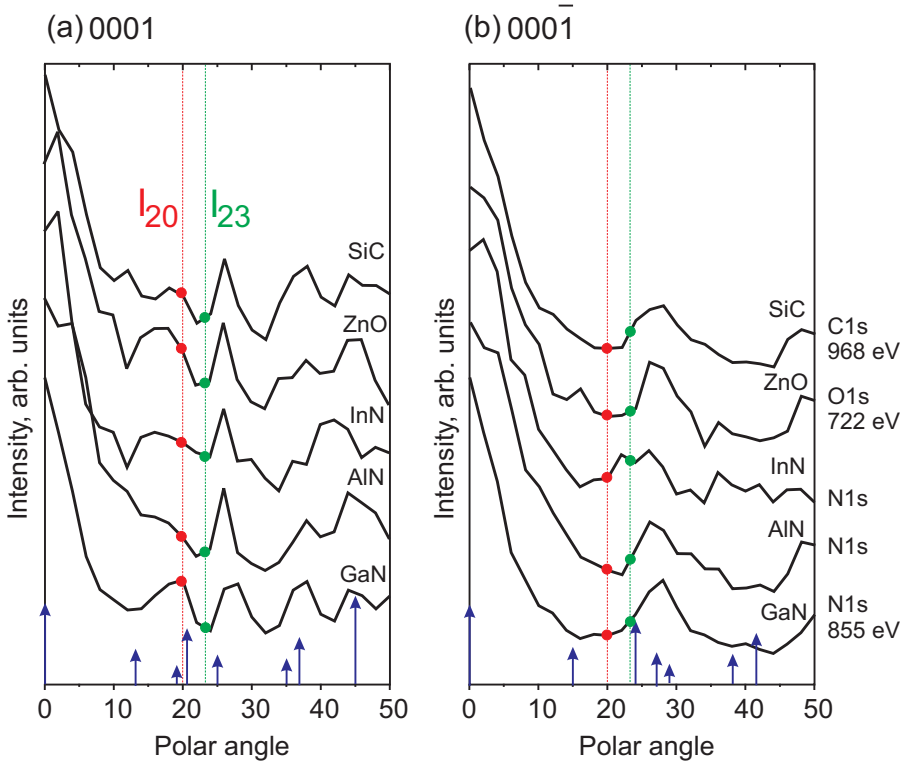

Fig. 2. Calculated polar plots of photoemission intensities emitted from polar surfaces of wurtzite semiconductors in the $(1\,0\,\bar{1}\,0)$ azimuthal plane: (a) from the cation-terminated surface, (b) from the anion-terminated surface. MgKα radiation is adopted for electron excitation from C 1s, N 1s and O 1s anion core levels, electron kinetic energies in eV are attached. Polar angles corresponding to the straightforward electron scattering are indicated by vertical arrows (the arrow lengths are exponentially decreased with the anion–cation distance).

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