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Size and orientation effect on the mechanical properties of $LiAlO_2$ single crystal

S.C. Tsai, H.C. Chen, J.C. Huang*, C.M. Chang, M.M.C. Chou

Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC

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ABSTRACT

The mechanical responses of $LiAlO_2$ single crystals on the (001) c-plane and (100) a-plane are examined by using nanoindentation and compression testing, extracting the millimeter-, micrometer-, and nanometer-scaled data. Apparent sample size effects on the yield stress are observed, increasing from 0.5 to 1 GPa in millimeter scale up to 11–14 GPa in nano-scale, as a result of flaw reduction, which can be rationalized by the Weibull statistics. Minor orientation effects are also observed. The c-sample possesses higher values than the a-sample in terms of modulus, Poisson's ratio, hardness and yield stress.

1. Introduction

Over the past few decades, scientific researchers raised a great deal of interests in the lithium aluminate, $LiAlO_2$ (LAO). The cell contains four molecules and the calculated density is 2.615 g/cm^3. γ-$LiAlO_2$ can crystallize in the tetragonal space group $P4_12_12$. The unit cell of this γ-$LiAlO_2$ crystal contains four formula units with lattice parameters $a=5.1687\pm0.0005$ Å and $c=6.2679\pm0.0006$ Å [1].

Owing to their high exciton binding energy, thermal conductivity and chemical stability, the direct wide-band-gap semiconductors such as ZnO and GaN have been widely studied, and applied in electrically pumped ultraviolet–blue light-emitting diodes, lasers, biosensor, and photon detectors [2–4]. γ-$LiAlO_2$ (100) is a substrate that allows the growth of pure m-plane GaN and ZnO films. The structural properties of the GaN or ZnO epilayers on various substrates have been explored, particularly with regard to its in-plane anisotropy. It has been demonstrated that GaN $(1\bar{1}00)$ layers of high phase-purity may be grown on γ-$LiAlO_2$ (100) [5]. It appears that the (100) surface of γ-$LiAlO_2$ is a promising substrate for growing heteroepitaxial layers of GaN and ZnO or other films in their $[10\bar{1}0]$ nonpolar direction [4,6–9].

With most interests and efforts were placed on the functional characteristics, the mechanical responses of this LAO crystal have rarely been studied. One previous report was aimed on the twinning deformation mechanism of γ-$LiAlO_2$ at low temperatures [10]. This current study follows that by examining the sample size and orientation effects at room temperature by using compression and nanoindentation testing. The size and orientation effects of LAO are considered to be important, since the modulus and strength mismatch between LAO and other heteroepitaxial layers such as GaN, ZnO or other thin film materials could induce mismatch internal stress or even dislocations or related defects along the interfaces during the thermal cycles of fabrication routines. The LAO can be applied as millimeter scaled crystals, or micrometer scaled thick films, or even nanometer scaled thin films in multilayerd devices. Thus, the mechanical data in millimeter, micrometer and nanometer scales are all needed in IC (integrated circuit) design. Meanwhile, the LAO crystals or films might be applied in various orientations, thus the orientation effects also need to be carefully explored. The joint systematic examination of size and orientation effects of LAO can provide very useful information for semiconductor and optoelectronic multilayerd device fields.

Size and orientation effects can be critical when LAO is applied for devices in micro- or nano-scales. The sample size effect considered in this study covers sample size from millimeter, micrometer, down to nanometer scale. And the orientation effect covers the c-sample (i.e., tests to be conducted on the (001) plane or along the [001] direction) and the a-sample (i.e., on the (100) plane or along the [100] direction).

In according to the deviation by Oliver-Pharr model [11,12], the Young's modulus of the sample, E_s, can be extracted by

$$E_r=\left[\left(\left(1-\nu_{tip}^2\right)/E_{tip}\right)+\left(\left(1-\nu_s^2\right)/E_s\right)\right]^{-1}, \quad (1)$$

* Corresponding author.
E-mail address: jacobc@mail.nsysu.edu.tw (J.C. Huang).

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where the E_r is the reduced Young's modulus, E_{tip} and ν_{tip} are the Young's modulus and Poisson's ratio of the diamond indenter tip. In this study, E_{tip} is about 1141 GPa and ν_{tip} is about 0.07. The Poisson's ratio plays an important role in both equations.

Since the mechanical behavior for both the c-sample and a-sample is intended to be examined, the individual theoretical Young's modulus, $E_{s,c}$ and $E_{s,\ a}$, and Poisson's ratio, $\nu_{s,c}$ and $\nu_{s,\ a}$, along the c-direction and a-direction need to be evaluated first, using the elastic compliance matrix for the LAO tetragonal structure,

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}. \tag{2}$$

The details have well been presented in text books. From the matrix for compliance and stiffness, the individual Young's modulus and Poisson's ratio along the c-direction and a-direction can be calculated.

2. Experimental section

The γ-$LiAlO_2$ single crystal rod measuring 50 mm in diameter was grown along the [100] direction by the Czochralski pulling technique [13]. The orientation of γ-$LiAlO_2$ were determined by XRD peak analyses (SIEMENS D5000 X-ray diffractometer with Cu K_α radiation λ=1.5406 Å). The mechanical properties of γ-$LiAlO_2$ were assessed by performing nanoindentation and compression tests. The nanoindentation and microcompression experiments were conducted by the MTS Nano-Indenter XP equipped with Berkovich tip for nanoindentaiton and flat-punch tip for micropillar compression. The nano-scaled hardness and modulus were obtained by the continuous stiffness measurement (CSM) mode and the nano-scaled and microcompression yield stress was conducted by the loading rate control (LRC) mode at 10^{-5} N/s. The approximate strain rate is estimated to be about $10^{-4}\ s^{-1}$. The millimeter scaled compression tests were done by the Instron 5582 universal testing machine at a quasi-state strain rate of $10^{-4}\ s^{-1}$.

Microcompression samples were prepared by using a dual beam SEM/FIB (scanning electron microscopy/focused ion beam) system, abbreviated as FIB below, following a method developed by Uchic et al. [14,15]. A conducting Au layer was coated on γ-$LiAlO_2$ for few nanometers in thickness to avoid the charging effect during FIB milling. Ga ion beam operated at 30 keV and 7–12 nA were initially directed perpendicular to the (001) (i.e., the c-sample) and (100) (i.e., the a-sample) of the γ-$LiAlO_2$ single crystals to mill a crater with a diameter of 40 µm and depth of 0.5 µm. Then, smaller currents ranged from 0.09 to 0.7 nA were used for the final milling or cleaning of the micro-pillars [16,17]. The final dimensions of micropillars prepared in this study were 2 µm in diameter and 4 µm in height. These pillar samples have a minor taper angle around 2°. The millimeter scaled compression rectangle rod samples measure 3 mm × 3 mm × 6 mm. The deformed samples were examined by scanning electron microscopy, JOEL JSM-6330.

3. Results and disscussion

Fig. 1 presents the XRD pattern showing a sharp peak of the γ-$LiAlO_2$ (004) planes located at 2θ=58.74° for the crystal cut from the c-plane (the c-sample). In parallel, the XRD pattern in Fig. 1 shows a sharp peak of the γ-$LiAlO_2$ (200) planes located at 2θ=34.71° for the crystal cut from the a-plane (the a-sample). The sharp and single peak confirms the accuracy of the plane cut from the γ-$LiAlO_2$ single crystal..

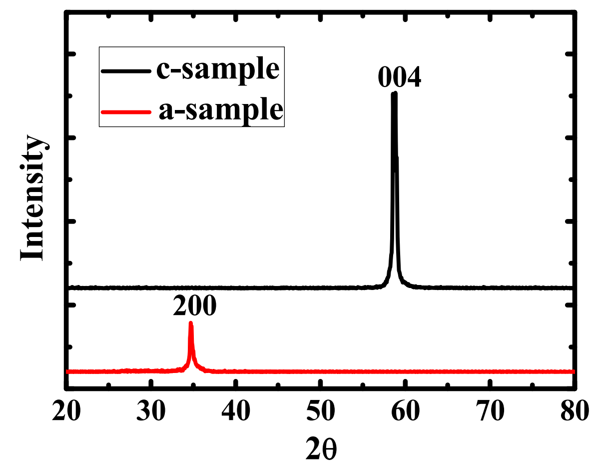

Fig. 1. XRD patterns of γ-$LiAlO_2$ (004) for the c-plane crystal and (200) for the a-plane crystal.

Before exploring the experimental measurements, the theoretical values calculated by the compliance and stiffness matrix need to be established in order to put into the equations to calculate the sample modulus/stress and Poisson's ratio for each plane or direction. For the γ-$LiAlO_2$ crystal at 26 °C, the elastic constants C_{11}=173.24, C_{12}=26.08, C_{13}=48.83, C_{33}=176.23, C_{44}=64.27 and C_{66}=35.53 GPa [18]. The stress ($\sigma_{ij}=C_{ij}\times\varepsilon_{ij}$, where σ is the stress and ε is the strain), can be calculated by filling in the elastic constants into Eq. (2). The Poisson's ratio along the c-direction equals $-C_{13}/(C_{11}+C_{12})$, resulting in a value of 0.24. In parallel, the Poisson's ratio along the a-direction equals $(C_{13}C_{13}-C_{11}C_{13})/(C_{11}{}^2+C_{12}C_{33})$, resulting in a value of 0.19, both listed in Table 1.

By inputting the above constants into the stiffness matrix S,

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{11} & S_{13} \\ S_{13} & S_{13} & S_{33} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{bmatrix}, \tag{3}$$

the theoretical value of the Young's modulus along the c-direction can simply be derived by $S_{33}{}^{-1}$, resulting in a value of 151 GPa, and the Young's modulus along the a-direction can be derived by $S_{11}{}^{-1}$, giving a value of 145 GPa, as also listed in Table 1.

The experimental work started from the millimeter scaled bulk compression samples, measuring in 3 × 3 mm in cross-section and 6 mm in height. The resulting modulus and yield stress data along the c-direction are 155 ± 5 GPa and 1.0 ± 0.2 GPa, respectively. In parallel, the measured modulus and yield stress data along the a-direction are 140 ± 4 GPa and 0.6 ± 0.1 GPa, respectively, as compared in Table 1. Note that the measured millimeter scaled modulus data are consistent with the calculated values by stress matrix. Also, both the modulus and stress along the c-direction are higher than those along the a-direction.

For the measurement in micrometer scale, the γ-$LiAlO_2$ micropillars measuring 2 µm in diameter and 4 µm in height were milled by FIB. The microcompression was repeated for three times, and the representative stress-strain curves along the c-direction and a-direction are shown in Fig. 2. The Young's modulus and flow stress of the slightly tapered micro-pillars are corrected. To examine the deformed morphology of the pillars, tests were interrupted at a load of 20 mN, representing the fully plastic conditions..