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High-temperature hardness of bulk single-crystal gallium nitride—in comparison with other wide-gap materials

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Abstract. The hardness of single-crystal gallium nitride of 500 μm thickness at elevated temperatures is measured and compared with those of other semiconductors. A Vickers indentation method was used to determine the hardness under an applied load of 0.5–5 N in the temperature range 20–1200 °C. The average hardness is 10.8 GPa at room temperature, which is comparable to that of Si. At elevated temperatures, GaN shows higher hardness than Si, GaAs, and ZnSe. A high mechanical stability for GaN at high temperature is deduced.

1. Introduction

GaN (gallium nitride) and its alloys appear promising as wide-band-gap, high-temperature semiconductor materials for application as blue- and ultraviolet-light-emitting devices and high-power/high-frequency devices [1]. Usually GaN materials are grown on various foreign substrates with lattice mismatch and significant differences in thermal expansion coefficient. Such hetero-epitaxial structures are inevitably accompanied by the introduction of various kinds of extended defect such as dislocations and prismatic stacking faults [2]. It is well recognized that the reduction in density of threading defects leads to improvement of optical and electrical properties of GaN [3]. Thus, efforts are being made in the controlling of film stress to reduce the occurrence of detrimental defects during GaN hetero-epitaxial growth to obtain high-performance devices. Understanding of the behaviour of dislocations in this material is indispensable.

The obstacle to conducting such an investigation has been the difficulty in growing crystals in a bulk form by the Bridgman and Czochralski techniques because of the high equilibrium vapour pressure of nitrogen (≈4 GPa) at the melting point. A few investigations are available on mechanical properties of GaN at room temperature (RT). Drory *et al* [4] measured the hardness and fracture toughness of GaN by means of a conventional hardness test. Suzuki and Takeuchi [5] reported the stacking fault energy of 20 mJ m^{-2} for dissociated dislocations induced by pulverization deformation. Nowak *et al* [6] evaluated the yield strength of GaN by means of nano-indentation. Maeda *et al* [7] observed the viscous motion of dislocations with recombination-enhanced glide under electron irradiation using a transmission electron microscope operating at 200 kV. Nevertheless, information on the mechanical strength of GaN at elevated temperature is important as a basis for the control of dislocation generation during crystal growth. Recently, Yonenaga *et al* [8] and Hong *et al* [9] reported the high-temperature hardness of bulk GaN grown by hydride vapour-phase epitaxy (HVPE).

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This paper reports the hardness of GaN at elevated temperature in comparison with those of other materials such as Si and GaAs including the typical wide-gap semiconductors α-SiC and ZnSe.

2. Experimental procedure

GaN single crystals were prepared from a high-quality GaN thick film grown on a two-inch-diameter (0001) sapphire substrate by using HVPE together with selective growth through SiO_2 windows by means of the facet-initiated epitaxial lateral overgrowth (FIELO) technique. The details of the growth procedure are given elsewhere [10]. Finally, the thick layer grown was removed from the substrate. As a result, crack-free GaN single crystals of 0.5 mm thickness with mirror-like surfaces were successfully obtained and were sufficiently thick to be regarded as being bulk material. The density of grown-in dislocations was as low as 10^7 cm^{-2} [11]. Hardness measurements on the crystals were carried out by the conventional Vickers indentation method using a pyramidal diamond indentor. The applied indentation load P was 0.5–5 N, and the dwell time 30 seconds, for every temperature tested in the range from room temperature to 1200 °C in a high-purity Ar-gas atmosphere. Four impressions were formed at every temperature for the Ga(0001) and N(000$\bar{1}$) basal-plane surfaces.

3. Results and discussion

Figures 1(a) and 1(b) show optical micrographs of the impression, formed for the N(000$\bar{1}$) surface of GaN, at RT. Impressions formed for the surfaces of the samples exhibited fracture characteristics for brittle materials with a pattern of radial cracks propagating from the impression corners at temperatures up to 100 °C, while more characteristic deformation with no cracks occurred at elevated temperature as seen in figure 1(c). At RT no crack could be observed under an applied load of 0.25 N.

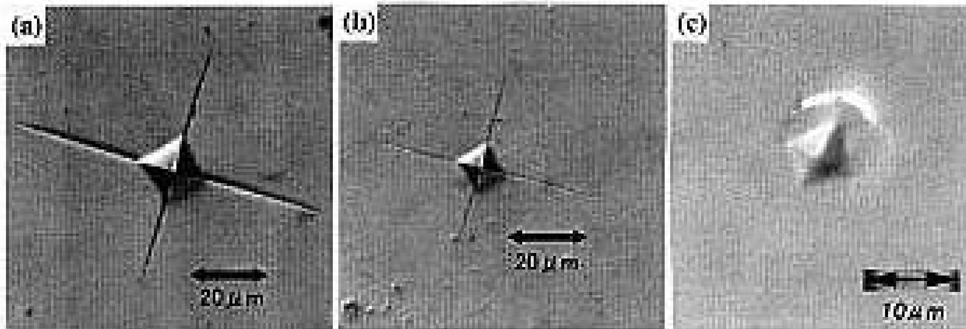

Figure 1. Optical micrographs of the Vickers impression on the N(000$\bar{1}$) surface of bulk crystal GaN (a) at room temperature with an applied load of 2 N and a dwell time of 30 s, (b) at room temperature with an applied load of 1 N and a dwell time of 30 s, and (c) at 200 °C with an applied load of 0.5 N and a dwell time of 30 s.

The hardness H_V was estimated from the load P and diagonal lengths $2a$, measured by optical microscopy, of the impression using the following relation:

$$H_V = P/(2a^2). \qquad (1)$$

The fracture toughness K_c was also determined from the radial crack length c:

$$K_c = \xi(E/H_V)^{1/2}(P/c^{3/2}) \qquad (2)$$

where E is Young's modulus and ξ is a calibration constant (=0.016) for brittle materials.

The hardnesses are almost comparable for the Ga(0001) and N(000$\bar{1}$) polar surfaces at all temperatures investigated. At RT the hardness of GaN is estimated to be 10.8 GPa under the applied load 0.5–3 N, about twice and ten times the values for GaAs and ZnSe, respectively. The measured hardness of (0001) surfaces of GaN is similar to those at 12 GPa and 12.3 GPa reported by Drory *et al* [4] and Hong *et al* [9], respectively. In their experiments the applied load was 2 or 1 N. The fracture toughness is estimated to be 1.1 MPa m$^{1/2}$ for the applied load range 0.5–5 N using equation (2) with $E = 295$ GPa, recently reported [6], which is also comparable to those given by Drory *et al* [4] and Hong *et al* [9]. Table 1 compares the hardness and fracture toughness of GaN together with those of various semiconductors and α-sapphire at RT [12–15]. The result suggests that the hardness of semiconductors is related to the bonding distance, as proposed by Sher *et al* [16].

Table 1. The Vickers hardness and fracture toughness for GaN and various semiconductors at room temperature or 300 °C [12–15] together with their bonding distances [17].

Material	Hardness (GPa)	Fracture toughness (MPa m$^{1/2}$)	Bonding distance (nm)
GaN(0001)	10.2	1.1	0.196
GaAs(111)	6.8	0.4 (reference [12])	0.245
ZnSe(111)	1.1	0.9 (reference [13])	0.245
Si(111)	12.0	0.7 (reference [14])	0.235
6H-SiC(0001)	22.9 (300 °C)	3.3 (reference [14])	0.188
α-Al_2O_3(0001)	28 (reference [15])	2.5 (reference [14])	0.192

Figure 2 shows the hardness H_V of GaN, obtained with an applied load of 0.5 N and a dwell time of 30 s, plotted against reciprocal temperature, in comparison with those of other material (111) or (0001) surfaces. Throughout the entire temperature range investigated, the hardness

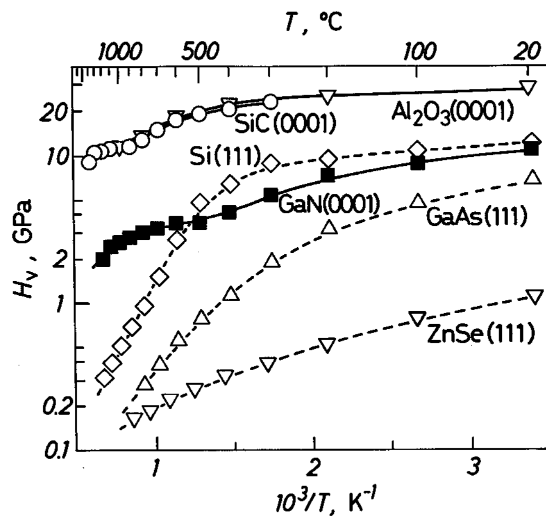

Figure 2. The Vickers hardness of bulk single-crystal GaN plotted against reciprocal temperature, with an applied load of 0.5 N and a dwell time of 30 s, together with those for Si, GaAs, ZnSe, and 6H-SiC. The hardness of sapphire obtained with an applied load of 2 N and a dwell time of 15 s is superimposed [12].

of GaN exhibits a gradual decrease from RT to 500 °C, then something of a plateau in the range from 500 to 1000 °C, and subsequently a steep decrease. This temperature-dependent tendency is similar to those of 6H-SiC and sapphire, with the similar hcp-based structure, although the temperature range and hardness magnitudes of SiC and sapphire are higher than those of GaN. The appearance of the plateau may be related to the operation of different slip systems in the crystal structure. It is found that GaN is harder than GaAs over the whole temperature range investigated and that at temperatures lower than 600 °C, the hardness of GaN is comparable to, or a little lower than, that of Si. In the latter temperature range, the phase transformation beneath the indentor may influence the hardness of Si, since the phase transformation pressure is ∼11.3 GPa. Surprisingly, up to about 1100 °C, GaN maintains its hardness and is harder than Si. Indeed, Si and GaAs exhibit a steep decrease in hardness from 500 °C and 200 °C, respectively, with increasing temperature, which indicates the beginning of macroscopic dislocation motion and plastic deformation. Thus, the results for GaN imply that this macroscopic dislocation motion and plastic deformation may start at around 1100 °C. Over the whole temperature range investigated, ZnSe is known to be less stable than GaN. A similar temperature dependence of the GaN hardness has been reported for $(11\bar{2}0)$ prism surfaces by Hong *et al* [9].

The results imply that GaN has a lower susceptibility to deformation during device processing at high temperatures as compared with Si, GaAs, ZnSe, and possibly other III–V and II–VI compounds except some nitrides. Unfortunately, the more complete physical understanding of hardness needed to derive the dynamic properties of dislocations is still lacking in the absence of adequate theory, and achieving this remains a task for the future. However, we believe that the present data provide a useful measure of material strength at elevated temperature. Further work is needed to determine the dislocation mobilities in GaN bulk crystals under a defined stress distribution, though the activation energy for the dislocation motion in GaN is empirically presumed to be 2 eV. Activation energies for dislocation motion have been shown to have a linear relationship with the band-gap energy dependent on the group of semiconductors, i.e., the elemental and IV–IV compounds, III–V compounds, and II–VI compounds [18].

4. Conclusions

The Vickers hardness for bulk single-crystal GaN was determined over the temperature range 20–1200 °C. The hardness of GaN is ≈10.8 GPa at RT and is comparable to that of Si at temperatures lower than 600 °C. Up to about 1100 °C, GaN maintains its hardness, being mechanically stable in comparison with Si, GaAs, and ZnSe.

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