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Hardness of bulk single-crystal GaN and AlN

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The hardness of single-crystal GaN and AlN of 0.5-mm-thickness was measured by the Vickers indentation method in the temperature range 20 - 1400°C. The hardness of GaN and AlN is 10.2 and 17.7 GPa, respectively, at room temperature. The nano-indentation hardness of single-crystal AlN was measured at room temperature as 18 GPa, harder than GaN and InN. Up to about 1100°C, GaN and AlN maintain its hardness similar to that of SiC and thus, a high mechanical stability for GaN and AlN at elevated temperatures is deduced. Yield strength of nitrides is discussed.

1 Introduction

III-V nitrides are finding applications such as in high-power/high-frequency devices, high-power switches, blue and ultraviolet light-emitting devices/photo-detectors, and chemically stable substrates for various materials. Many of the physical properties required for characterizing the material have been determined in the past, however, up to now, comparatively little is known about the mechanical properties of these materials. Mechanical characteristics such as elastic constants, yield strength at elevated temperatures, etc. are crucial for controlling dislocation generation and plastic deformation during crystal growth and device processing. The reduction in dislocation density is expected to result in improvement of the optical and electrical performance of nitrides. It is also necessary to solve the problems of residual stress/strain for the potential optical and electronic properties in a device design. A considerable effort has already been made to evaluate the elastic stiffness coefficients of nitride by *ab-inito* calculations [1] [2] [3]. The difficulty of preparation of bulk III-V nitride crystals was a limiting factor in obtaining this information. Recently, some research groups have succeeded in growing thick nitride films, which can be regarded as a bulk material, by using a hydride vapor phase epitaxy (HVPE) technique [4] [5].

Hardness is a material parameter indicating resistance to elastic/plastic deformation. Thus, various indentation hardness methods are widely used in the study of mechanical properties of materials over a wide range of size scales, and recently nano-indentation is of growing interest in clarifying the mechanical properties for small crystals and especially for thin films on substrates.

This paper reports the hardness of bulk single-crystal GaN and AlN at room temperature (RT) and at elevated temperatures. The nano-indentation hardness of AlN at RT is also determined. The results are compared with those of other nitrides InN and InGaN together with the other typical semiconductors Si, Ge, GaP, and GaAs, including the wide-gap semiconductors ZnSe and 6H-SiC.

2 Experimental Details

GaN and AlN single crystals were prepared from high-quality thick films grown on substrates by the HVPE technique, the details of which were described elsewhere [4] [5]. After the HVPE process, the substrates were removed by chemical etching. As a result, crack-free GaN and AlN single crystals of 0.5 mm thickness with mirror like surfaces were successfully obtained. The grown-in dislocation density in the GaN crystals was as low as 10^7 cm^{-2}, while that in the AlN crystals was approximately 10^8 - 10^9 cm^{-2}.

Hardness measurements were carried out on the (0001) surfaces of the crystals using the conventional Vickers micro-indentation method with a pyramidal diamond indenter. The applied indentation load was 0.5 - 5 N. The dwell time was 30 s for every temperature tested in the range from room temperature to 1400°C in a high-purity Ar gas atmosphere. The surfaces of GaN and AlN were very smooth after indentation at the highest temperatures as determined by observation with an optical microscope. Therefore the effect of thermal decomposition of the nitride samples seems not to be serious enough to affect the experimental results. The nano-indentation hardness of AlN was measured on the (0001) surface of the crystals using a commercial Nanoindenter UMIS-2000 (XSIRO, Australia) equipped with a sharp triangular diamond indenter (Berkovich-type) in a continuous depth-sensing mode. The details of the experimental procedure are described elsewhere [6] [7] [8].

3 Results and Discussion

3.1 Room temperature hardness

At RT indentations formed on the basal plane surfaces of the crystals sometimes exhibited fracture characteristics for brittle materials with radial cracks propagating from the impression corners under an applied load of more than 2 N. The micro-hardness is almost comparable for the (0001)/(111) and $(000\bar{1})/(\overline{111})$ polar surfaces of the crystals with the hcp-/cubic-based structure at all temperatures investigated.

Figure 1 shows the micro-hardness of GaN and AlN obtained with an applied load of 0.5 N and dwell time of 30 s plotted against the reciprocal temperature together with the values for Si, Ge, GaP, GaAs, 6H-SiC, and ZnSe. As seen in Figure 1, at RT the hardness of GaN is 10.8 GPa, about twice and ten times the value of GaAs (6.8 GPa) and ZnSe (1.1 GPa), respectively. Similar values of GaN hardness have been reported by other research groups with different source materials, that is, 12 GPa and 12.3 GPa are given by Drory et al. [9] on GaN grown under high pressure and by Hong et al. [10] on HVPE-grown GaN, respectively. The micro-hardness of AlN at RT is 17.7 GPa, which is similar to or higher than 12 GPa (Knoop hardness) [11] and 14 GPa [12], meanwhile the nano-hardness is 18 GPa. As evident in the table, AlN is harder than GaN while softer than 6H-SiC [13]. ZnSe, one of the expected wide-gap semiconductors, is much softer than other materials.

Table 1 shows the micro- and nano-hardness of wurtzite-type III-V nitrides at room temperature, together with those of Si [14] [15] [16] [17]. As evident in the table, AlN shows a harder micro-hardness than GaN, meanwhile the magnitude of nano-hardness is close to each other. That is, the hardness of GaN determined by using a nano-indentation method is much higher than that by conventional micro-indentation method. Here, it should be noted that the hardness of Si at low temperature around RT is affected by the phase transformation that occurs at a pressure of about 11.3 GPa [18] beneath the indenter. AlN has been reported experimentally to show a wurtzite-to-rock salt transition around 22.9 GPa at room temperature [19]. The value is close to that obtained by both the indentation methods in the present study. Contrarily, the wurtzite-to-rock salt transition pressure in GaN is reported to be around 52 GPa [20]. Thus, we may reflect the phase transition for determining the hardness of a material in the nano-indentation measurement since the local stress concentration for determining the hardness becomes large under and/or around the indenter.

The mechanical properties of InN [15] and $In_{0.1}Ga_{0.9}N$ [16] are available only on the nano-indentation hardness of thin films grown on sapphire substrates. The growth sources of these nitrides are different and the grown-in dislocation density, probably higher than 10^9 cm^{-2}, and the film thickness on the substrates are not the same. Thus, a direct comparison of the mechanical hardness is hard for quantitative discussion, however at least InN is known to be softer than AlN and GaN in comparison of the hardness among III-V nitrides. The hardness of semiconductors is often suggested to be dependent on the bonding distance or shear modulus. Indeed, InN has extremely small shear modulus and large bonding distance in comparison with AlN and GaN. $In_{0.1}Ga_{0.9}N$ alloy seems to be much harder than InN and GaN. Generally alloy semiconductors as GaAsP and InAsP are known to show higher mechanical strength than the component compound semiconductors GaAs and GaP, InAs and InP, respectively, due to the solid solution hardening as reported by Yonenaga and Sumino [21] [22]. The detailed discussion based on the data from bulk or thick crystals/alloys without any effect from substrates is a task for the future.

3.2 High temperature hardness

As seen in Figure 1, throughout the entire temperature range investigated, the hardness of GaN, AlN, and SiC exhibits a gradual decrease from RT to 700°C, then something resembling a plateau in the range to around 1000°C, and subsequently, a steep decrease. This temperature-dependent tendency is common in semiconductors which adopt the hexagonal-structure, although the temperature range and hardness magnitudes of SiC are higher than that of GaN and AlN. The plateau may appear in relation to the operation of different slip systems in the crystal structure. It is found that in the entire temperature range investigated the hardness magnitudes of AlN are greater than those of GaN but lower than those of SiC.

Most surprising is that up to about 1100°C, GaN and AlN maintain their hardness and are harder than Si. Indeed, Si, Ge, GaP, and GaAs exhibit a steep decrease in hardness from 500°C and 200°C, respectively, with an increase in the temperature, which indicates the beginning of macroscopic dislocation motion and plastic deformation [23] [24]. The present results indicate that GaN and AlN may start the macroscopic dislocation motion and plastic deformation of at around 1100°C similar to SiC, but in contrast to Si, Ge, GaP, GaAs, and possibly other III-V compounds with the sphalerite structure. Over the whole temperature range investigated, ZnSe is known to be most unstable mechanically in the materials. Probably ZnSe can easily deform around RT.

The present results imply that GaN and AlN have a lower susceptibility to deformation during device processing at high temperatures. Thus, the results for GaN and AlN imply that this macroscopic dislocation motion and plastic deformation may start at approximately 1000°C. Recently the present author succeeded in determining the yield strength of bulk single crystal of GaN to be around 100-200 MPa at 900°C [25].

Figure 2 shows the relation between the Vickers hardness H_v and yield stress of the semiconductor crystals at high temperatures. For cubic type semiconductors as Si [23], Ge [26], GaP [27], and GaAs [24], the hardness and yield stress are at 700°C while for GaN and SiC [28] those are at 1000°C. At respective temperatures, the hardness and yield strength show a good correlation with the same slope. Though a more detailed understanding of the relation is needed in future, from the relationship we can deduce the yield strength of AlN to be ~ 300 MPa at 1000°C.

4 Conclusion

The Vickers hardness of bulk single crystal GaN and AlN of 0.5 mm thickness was determined in the temperature range 20 - 1400°C in comparison with that of SiC, Si, Ge, GaP, GaAs, and ZnSe. The hardness of AlN and GaN is 17.7 and 10.2 GPa, respectively, at room temperature. The nano-indentation hardness of AlN was also measured tat RT as 18 GPa. The hardnesses at RT were compared with that of other nitrides InN and InGaN. AlN and GaN show a decrease in hardness, originating into the beginning of macroscopic dislocation motion and plastic deformation, only at temperature 1200°C. The results imply that these crystals have a smaller susceptibility to deformation during device processing at high temperatures as compared with Si, Ge, GaP, GaAs, and ZnSe. The yield strength of AlN is deduced to be about 300 MPa from the relationship between the yield stress and hardness of semiconductors.

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FIGURES

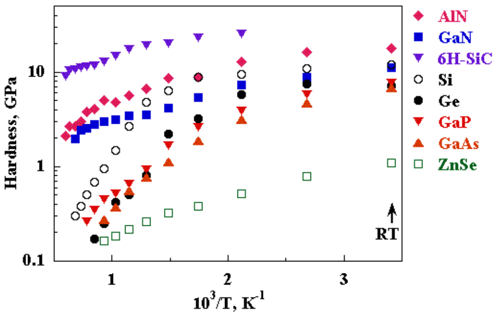

Figure 1. Vickers hardness of bulk single-crystal GaN and AlN plotted against reciprocal temperature, with an applied load of 0.5 N and dwell time of 30 s, together with those of 6H-SiC, Si, Ge, GaP, GaAs, and ZnSe. RT means room temperature.

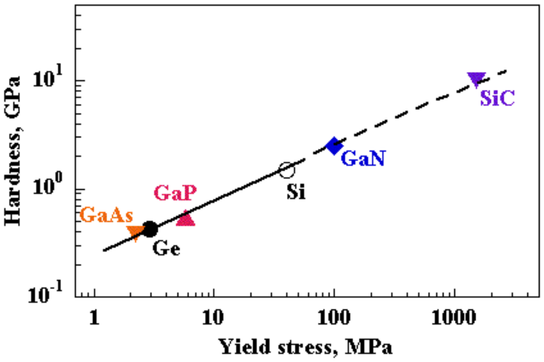

Figure 2. Vickers hardness plotted against the yield strength at 700°C for cubic type semiconductors as Si [23], Ge [26], GaP [27], and GaAs [24], and at 1000°C for GaN [25] and SiC [28]. Here, the yield strength of SiC is extrapolated based on the measured results in the temperature range 1300-1800°C.

TABLES

Table 1. Hardness of III-V nitrides at room temperature together with phase transition pressure, bonding distance, and shear modulus. InN and $In_{0.1}Ga_{0.9}N$ grown on sapphire substrate.

Crystal	Micro-hardness (GPa)	Nano-hardness (GPa)	Phase transition pressure (GPa)	Bonding distance (nm)	Shear modulus (GPa)
AlN	17.7	18	22.9 [19]	0.192	154 [8]
GaN	10.2	18-20 [14]	52 [20]	0.196	121 [29]
InN on sapphire		11.2 [15]	15 [20]	0.214	43 [30]
$In_{0.1}Ga_{0.9}N$ on sapphire		52 [16]			
Si	12.0	14 [17]	11.3 [18]	0.235	60.5