

High-temperature strength of III–V nitride crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 12947

(<http://iopscience.iop.org/0953-8984/14/48/336>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 19:14

Please note that [terms and conditions apply](#).

High-temperature strength of III–V nitride crystals

I Yonenaga

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Received 27 September 2002

Published 22 November 2002

Online at stacks.iop.org/JPhysCM/14/12947

Abstract

The hardness of AlN and GaN bulk crystals was investigated in the temperature range 20–1400 °C by the Vickers indentation technique. The hardnesses of GaN and AlN at room temperature are 10.8 and 17.7 GPa, respectively. With increasing temperature the hardness shows a gradual decrease and then a steep decrease from around 1000 °C, which indicates the beginning of macroscopic dislocation motion and plastic deformation. The yield strength of GaN bulk crystals determined directly by means of compressive deformation is around 100–200 MPa in the temperature range 900–1000 °C, i.e. similar to that of α -SiC and much higher than those of Si, Ge, GaP, GaAs, InP and InAs. On the basis of the observed temperature dependence of yield stress, the activation energy for dislocation motion at elevated temperatures in GaN is deduced.

1. Introduction

Knowledge of the mechanical strength of semiconductors at elevated temperatures is essentially important as a basis for the control of dislocation generation and plastic deformation during crystal growth and device processing. GaN and AlN III–V nitrides and alloys have attracted keen interest recently as wide-band-gap semiconductors for applications in e.g. high-power or high-frequency devices, high-power switches, blue- and ultraviolet light-emitting devices, photo-detectors and chemically stable substrates. In addition, these materials are expected to be mechanically stable and able to operate at high temperatures. Characteristic features for a variety of applications have been determined in the past. However, up to now, far less has been known on the mechanical properties of these nitrides. It is also necessary to balance the potentials of optical and electronic properties of such materials with lattice mismatch in a device design. Understanding how dislocations behave under stress is very important if one is to clarify the elementary mechanism of dislocation glide in semiconductors.

This paper reports on the hardness and mechanical strength of the III–V nitride bulk crystals GaN and AlN at elevated temperatures in comparison with those of wide-band-gap, elemental, III–V compound and II–VI compound semiconductors.

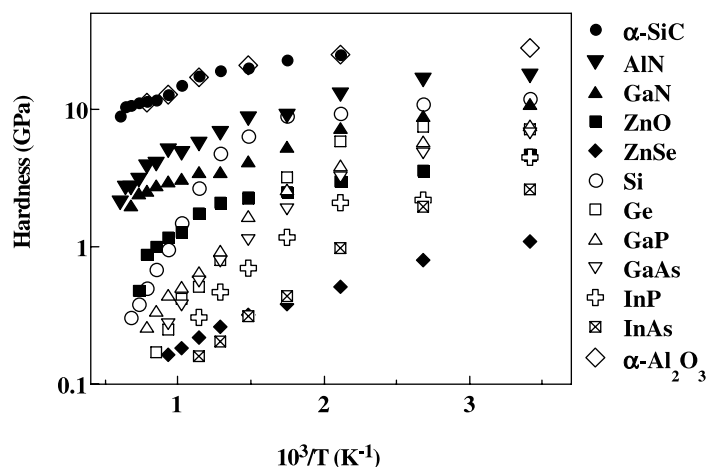


Figure 1. Vickers indentation hardness of single crystals of the wide-band-gap semiconductors α -SiC, AlN, GaN, ZnO and ZnSe plotted against reciprocal temperature, together with those of Si, Ge, GaP, GaAs, InP and InAs. Data on the hardness of α -Al₂O₃ at various temperatures reported by Farber *et al* [6] are superimposed.

2. High-temperature hardness of GaN and AlN

The hardnesses of single-crystal GaN and AlN, 0.5 mm thick, in the temperature range 20–1400 °C were measured by the Vickers indentation method in comparison with those of α -SiC, ZnO and ZnSe. GaN and AlN single crystals were prepared from high-quality thick film grown on substrates by the hydride vapour phase epitaxy (HVPE) technique [1, 2].

Figure 1 shows the hardnesses of α -SiC, GaN, AlN, ZnO and ZnSe, obtained with an applied load of 0.5 N and dwell time of 30 s, plotted against reciprocal temperature together with the values for Si, Ge, GaP, GaAs, InP, InAs and α -Al₂O₃ [3–7]. At room temperature (RT), indentations formed on the basal plane surfaces of the GaN and AlN 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 hardnesses are almost comparable for the opposite polar (0001)/(111) and (000 $\bar{1}$)/($\bar{1}\bar{1}\bar{1}$) surfaces of such crystals with the hcp/cubic-based structure at all temperatures investigated. As seen in figure 1, at RT the hardness of GaN is 10.8 GPa, about twice and ten times the values for GaAs and ZnSe, respectively. The hardnesses of AlN and ZnO at RT are 17.7 and 4.7 GPa, respectively. The hardness of ZnSe at RT is found to be 1.1 GPa: it is much softer than the other materials investigated.

Over the whole temperature range investigated, the hardnesses of α -SiC, GaN, AlN and ZnO exhibit a gradual decrease from RT to around 600 °C, then something of a plateau in the range to around 1000 °C and subsequently a steep decrease. This temperature-dependent behaviour is also shown by those semiconductors which have a hcp-based structure, although the temperature range and hardness magnitudes of α -SiC or α -Al₂O₃ are higher than those of AlN and GaN. The plateau may appear in relation to the operation of different slip systems in the crystal structure. It is found that over the whole temperature range investigated the hardness magnitudes of ZnO are smaller than those of α -SiC, AlN and GaN. It is surprising that up to about 1100 °C GaN and AlN maintain their hardness and are harder than Si. Indeed, Si and GaAs exhibit a steep decrease in hardness from 500 and 200 °C, respectively, with

increase in temperature, which indicates the onset of macroscopic dislocation motion and plastic deformation. The present results indicate that the macroscopic dislocation motion and plastic deformation of α -SiC, GaN and AlN may start at around 1100 °C. Over the whole temperature range investigated, ZnSe is known to be the most thermomechanically unstable material. From the results it is found that α -SiC, GaN and AlN have a lower susceptibility to deformation during device processing at elevated temperatures than Si, Ge, GaP, GaAs, InP, InAs, ZnSe and possibly other III–V and II–VI compounds with the zinc-blende structure.

3. Yield strength and dislocation mobility in plastically deformed bulk single-crystal GaN

Rectangular specimens for compression testing, of approximately $1.0 \times 1.0 \times 3.6 \text{ mm}^3$ in size, were cut out from a bulk single crystal with n-type carrier concentration of $5 \times 10^{18} \text{ cm}^{-3}$ grown as free-standing substrates by the HVPE technique [8]. The density of grown-in dislocations was about 10^5 cm^{-2} . The compression axis was inclined at 45° to the $[11\bar{2}0]$ direction with one side surface parallel to the (0001) basal plane.

Specimens deformed at temperatures higher than 900 °C did not show brittle fracture under the extremely high compressive stress [9]. Stress–strain curves at all temperatures were characterized by an apparent elastic increase in the stress, a smooth yield behaviour and a subsequent gradual increase in the stress with strain, i.e. plastic deformation. A stress drop in the yield region, typical for various elemental and compound semiconductors, was not observed. The features are rather similar to those of α -SiC deformed at high temperature [10]. The yield stress and flow stress decrease with increasing temperature. The most striking feature of the stress–strain behaviour is the extremely high levels of yield and flow stresses of around 100–200 MPa, even at 1000 °C. This is in good agreement with the results on the high mechanical stability of GaN obtained from the Vickers indentation tests as shown in the preceding section.

The yield stress τ_y of GaN is plotted against reciprocal temperature in figure 2 for deformation measurements carried out under a shear strain rate of $1.8 \times 10^{-4} \text{ s}^{-1}$, together with the (lower) yield stresses of Si [11, 12], Ge [13], GaP [14], GaAs [15], InP [16], InAs [16] and α -SiC [17]. The yield stress of GaN is more than two orders of magnitude higher than that of Si, Ge and the other compound semiconductors, and is slightly higher than that of α -SiC with basal slip.

Generally, the yield stress of a semiconductor crystal is described as a function of temperature T and strain rate $\dot{\epsilon}$ by the following empirical equation [16, 18]:

$$\tau_y = A\dot{\epsilon}^{1/n} \exp(U/k_B T), \quad (1)$$

where A , n and U are constants and k_B is the Boltzmann constant. The magnitude of U determined experimentally from the temperature dependence of the yield stress of GaN is $0.67 \pm 0.05 \text{ eV}$.

In semiconductor crystals, the dislocation velocity v is described using the following empirical equation as a function of the stress τ and temperature T :

$$v = v_0(\tau/\tau_0)^m \exp(-Q/k_B T), \quad (2)$$

where $\tau_0 = 1 \text{ MPa}$. The constants v_0 , m and Q are determined experimentally for various semiconductors [18, 19]. On the basis of the collective motion of microscopic dislocations that control the rate of the macroscopic deformation of crystals [16, 18, 19], the constants m and Q are related to n and U in equation (1) through the following equations:

$$n = m + 2, \quad Q = U^*(m + 2). \quad (3)$$

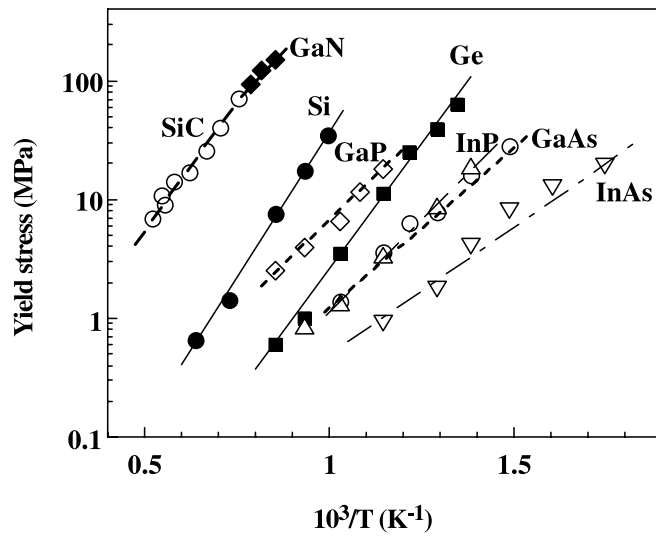


Figure 2. Yield stresses of GaN crystals plotted against reciprocal temperature for deformation under a strain rate of $1.8 \times 10^{-4} \text{ s}^{-1}$, in comparison with those of Si [11, 12], Ge [13], GaP [14], GaAs [15], InP [16], InAs [16] and α -SiC [17].

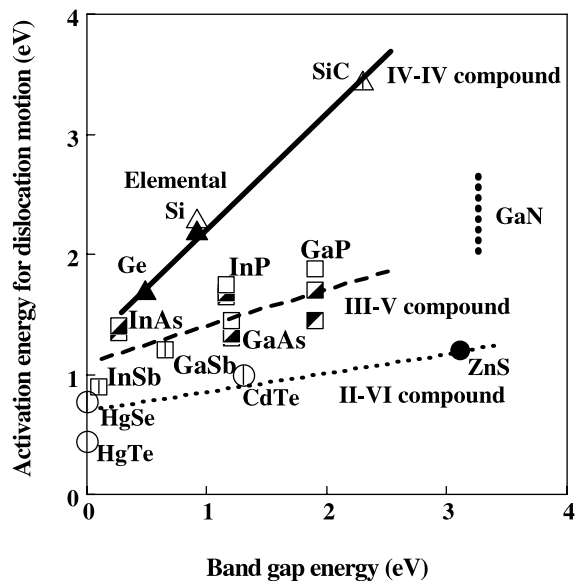


Figure 3. Activation energy for the dislocation motion as a function of the band-gap energy at $0.6 T_m$ (T_m : melting temperature) for various groups of semiconductors [19]. The estimated activation energy for GaN is superimposed.

The parameter m may be determined from the parameter n obtained from the strain-rate dependence of the yield stress, though in the present study this parameter has not been obtained because of the limitation of samples. Generally m is known experimentally to be 1–2 for semiconductor crystals [18, 19]. If the relations remain valid for GaN, then it can be presumed that the magnitude of Q is 2–2.7 eV.

In phenomenological terms, the activation energy Q for dislocation motion increases linearly with the band-gap energy of a number of semiconductors such as the elemental and IV–IV compounds, III–V compounds and II–IV compounds as seen in figure 3 [19]. The estimated magnitude of Q for GaN seems to fit well with the behaviour of the III–V compound group. Further work on the direct measurement of the mobility of isolated dislocations within bulk GaN crystals under a defined stress distribution is a task for the future, including detailed analysis of the dislocation structure. That would be a step towards clarifying the physical process of dislocation glide in semiconductor crystals.

Acknowledgments

The author is grateful to Professor P Pirouz of Casewestern Reserve University for supplying the SiC crystals, to Dr V Dmitriev of TDI, Inc., USA, for the AlN crystals, to Dr A Usui of NEC Corporation and Dr K Motoki of Sumitomo Electric Industries Ltd for the GaN crystals.

References

- [1] Usui A, Sunakawa H, Sakai A and Yamaguchi A A 1997 *Japan. J. Appl. Phys.* **36** L899
- [2] Nikolaev A, Nikitina I, Zubrilov A, Mynbaeva M, Melnik Y and Dmitriev V 2000 *Mater. Res. Soc. Symp. Proc.* **595** W6.5.1
- [3] Yonenaga I, Hoshi T and Usui A 2000 *Japan. J. Appl. Phys.* **39** L200
- [4] Yonenaga I, Hoshi T and Usui A 2000 *J. Phys.: Condens. Matter* **12** 10319
- [5] Yonenaga I, Nikolaev A, Melnik Y and Dmitriev V 2001 *Japan. J. Appl. Phys.* **40** L426
- [6] Farber B Ya, Yoon S Y, Lagerlöf K P D and Heuer A H 1993 *Phys. Status Solidi a* **137** 485
- [7] Yonenaga I 2001 *Physica B* **308–310** 1150
- [8] Motoki K, Okahisa T, Matsumoto N, Matsushima M, Kimura H, Kasa H, Takemoto K, Uematsu K, Hirano T, Nakayama M, Nakahata S, Ueno M, Hara D, Kumagai Y, Koukitsu A and Seki H 2001 *Japan. J. Appl. Phys.* **40** L140
- [9] Yonenaga I and Motoki K 2001 *J. Appl. Phys.* **90** 6539
- [10] Samant A V, Zhou W L and Pirouz P 1998 *Phys. Status Solidi a* **166** 155
- [11] Yonenaga I and Sumino K 1978 *Phys. Status Solidi a* **50** 685
- [12] Yonenaga I 1996 *J. Electrochem. Soc.* **143** L716
- [13] Yonenaga I 1999 *J. Mater. Sci., Mater. Electron.* **10** 329
- [14] Yonenaga I and Sumino K 1989 *J. Mater. Res.* **4** 355
- [15] Yonenaga I, Onose U and Sumino K 1987 *J. Mater. Res.* **2** 252
- [16] Yonenaga I and Sumino K 1992 *Phys. Status Solidi a* **131** 663
- [17] Fujita S, Maeda K and Hyodo S 1987 *Phil. Mag. A* **55** 203
- [18] Yonenaga I 1997 *J. Physique III* **7** 1435
- [19] Yonenaga I 1998 *J. Appl. Phys.* **84** 4209