

NANOINDENTATION RESPONSE OF SEMICONDUCTORS

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Abstract

The paper reviews the nanoindentation behaviour of semiconductors under concentrated load. We consider first, fundamental aspects regarding the mechanical resistance to contact loading of semiconductor single crystals (indentation strain, hardness-yield stress relationship). Then, the paper summarizes recent studies regarding nanoindentation structure and geometrical size effect.

1. Introduction

Mechanical properties of semiconductors at nanometre scales involved in devices are of utmost importance for optoelectronic applications [1, 2]. In that field, the nanoindentation technique has proved to be of great importance as the probe size can be scaled to the studied object adjusting the load applied to the indenter. Furthermore, because of the low-load range available with this technique, formation of cracks during the deformation can be avoided. This allows carrying out extensive studies in the elastic-plastic regime (that is, below the brittle-ductile transition, BDT). Unfortunately, nanoindentation is very difficult to perform at process temperatures [3, 4] and most studies are reported only at room temperature (RT) experiments. For the past two decades, transmission electron microscopy (TEM) has been extensively used to investigate the plastic-zone structure and dislocation arrangement. A survey of the literature shows that GaAs, unlike the other III-V semiconductors, showed emphasized polar character of the rosette [4-11]. In fact, in GaAs, microtwins and partial dislocations have been reported mostly in only one of the rosette arms. However, the character of the dislocations present in the related arms has been controversial. Another important issue regarding surface mechanics is the geometrical size effects. Indentation mechanics was developed for semi-infinite half space. Once the size of the object decreases, the mechanical response is expected to be affected. In a first step, the mechanical behaviour of homogeneous bulks (InP, GaAs) is reported and reviewed; the representative strain and flow stress, the effect of crystal polarity and composition (doping) will be illustrated and discussed. In a second step, we address the influence of size on the mechanical behaviour taking the case of a wall-patterned GaAs surfaces elaborated by photolithography.

2. Hardness, yield stress, and representative flow stress

Hardness measures the resistance to contact loading and is calculated as a mean pressure over the contact

$$H = F_m/A_c, \quad (1)$$

where F_m is the maximum load applied on the indenter, A_c is the contact area. It should be noted that hardness values obtained from instrumented nanoindentation and microindentation may differ significantly and this phenomenon is invoked as indentation-size effect (ISE). This phenomenon has been studied extensively while TEM has shown very useful to determine flow stress from plastic zone extension (see below). For elastic perfectly plastic materials, hardness is generally assumed to be three times the yield stress Y [12, 13]

$$H = 3 Y. \quad (2a)$$

These relationships can be extended to strain-hardening materials with good approximation when Y is replaced by the representative flow stress Y_R measured in simple compression at the representative strain ϵ_R [13]

$$H = 3 Y_R = 3 Y(\epsilon_R). \quad (2b)$$

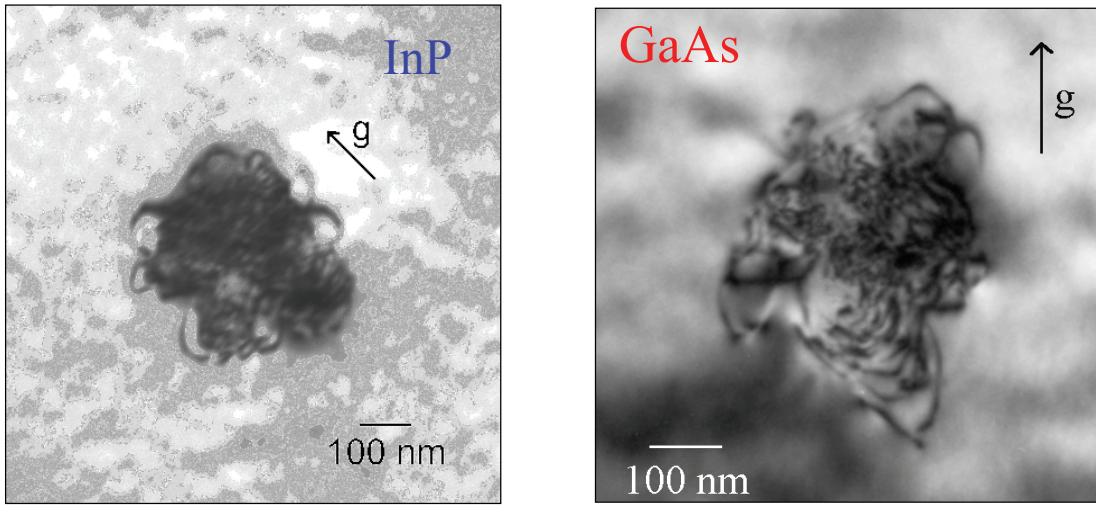


Fig. 1. TEM plan views of the indent site made at room temperature in undoped bulk (001)InP under 0.26 mN (left) and in undoped bulk (001)GaAs under 0.28 mN (right); $g = 220$.

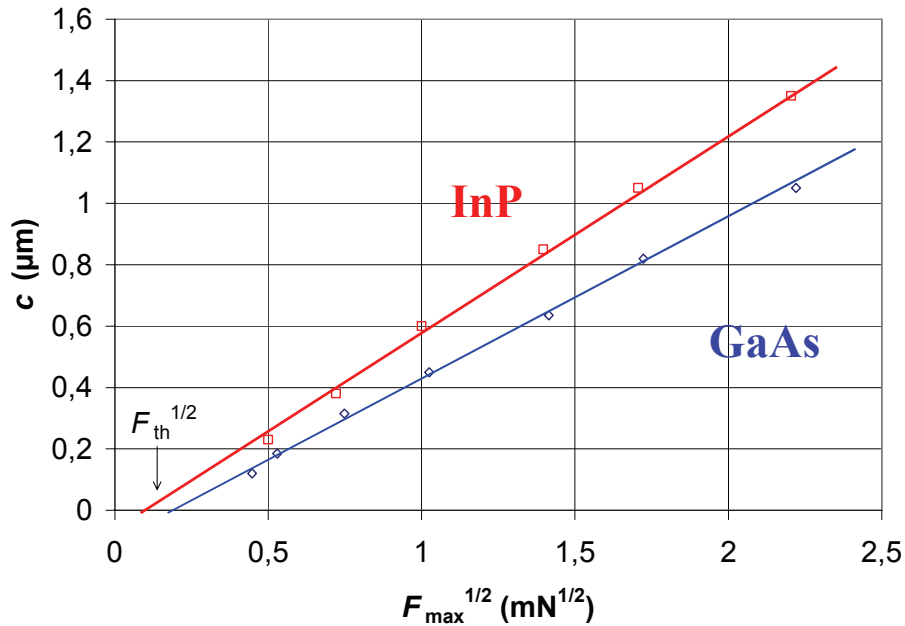


Fig. 2. Plastic-zone radius c as a function of the square root of the maximum load F_m . F_m was measured on the loading curves. The central plastic-zone radius was determined on TEM plan views.

Under a conical indenter the representative strain $\varepsilon_R = 0.2 \tan \beta$ remains unchanged (assuming a perfect sharpness of the tip, β being the angle between the original surface and the flank of a conical indenter), property that is often referred as self-similarity or auto-similarity. The self-similarity of the strain field under a conical indenter is to be attributed to the geometric similarity of the tip ($A_c \sim h_c^2$ where h_c is the contact depth). Self-similarity is also assumed for non-axisymmetric tips like Berkovich and Vickers ones. β is then the angle between the original surface and the flank of a conical indenter with equivalent aspect ratio. For instance, for the Vickers and Berkovich tips which are most commonly used, the contact area is $A_c = 24.5 h_c^2$ so that β is to be taken as 19° and ε_R is about 7.2%. This value corresponds to a mean value over the plastic zone since strain reaches 28% at tip extremity (as shown on a GaAs/GaAlAs superlattice [14]). In the literature, it must be said that there has been some confusion between Eqs. (2), which were used regardless of their domain of validity. However, the aperture of the tips commonly used by our community is generally large so that the representative strain is below 8%, which for low strain-hardening materials leads to $Y \sim Y_R$. Nonetheless, sharp cube-corner tips are now being employed to lower the plastic onset and, hence, to deform the specimens under slighter loads. For such a tip, Eqs. (2) should be used more carefully.

Following Johnson's cavity model [13], the representative flow stress Y_R of a material can be determined measuring the plastic zone radius c as a function of the maximum load F_m , applied to the indenter using Eq. 3 [15]

$$Y_R = \frac{3}{2\pi} \frac{F_m}{c^2}. \quad (3)$$

This relation is established under full load balancing the radial forces at the elastic-plastic boundary [15]. The proper use of Eq. (3) supposes that light indenting loads are applied to the specimen in order to avoid fracture and remain in the plastic regime. This is possible using the nanoindentation technique. Fig. 2 plots the central-plastic-zone size c as determined from TEM plan views as a function of the square root of the maximum load $\sqrt{F_m}$ measured for two single crystals (InP, GaAs). c is found to increase linearly with $\sqrt{F_m}$ as expected from Eq. (3) and allows for flow-stress values Y_R to be determined (2 and 3 GPa for InP and GaAs, respectively). The ratio between the hardness and the flow stress was determined to be close to 3 in a good agreement with Ref. [13]. It should be noted that AFM can also be employed to determine the plastic-zone size measuring the topography of the indent proximity [16, 17]. In that case, the plastic-zone size is estimated from the upset region or pile-up [16]. Except for very small indents where plastic recovery was observed, the upset-zone radius determined by AFM shows also a square-root dependence on load [16]. It should be noted that TEM and AFM yield different information. TEM reveals complex dislocation arrangements showing stacking faults as well as perfect dislocations (see section 3). Under nanoindentation we observe the beginning of the formation of rosette arms that have been reported under microindentation [4, 5]. As discussed in detail below, these are constituted by stacking faults arranged in microtwins, while their extremities show perfect dislocations with Burgers vector b parallel to the indented (001) surface and arm directions [4, 5]. Perfect dislocations with b parallel to the surface do not produce any upset of the original surface and, hence, cannot be detected by AFM contrary to partials. While employing TEM, we suggest considering the central-plastic zone only, which expands similarly to Johnson's cavity and plays a predominant role in the mechanical response as shown in more detail in section 4. The anisotropic character of the plastic flow can instead be captured considering the rosette arms as discussed in section 3.

3. Nanoindentation structure

Figures 3 and 4 show TEM images of indentations obtained in n- and p- heavily doped (001) GaAs (n-doped Si: $1-4 \cdot 10^{18}$ at. cm^{-3} , p-doped Zn: $2-5 \cdot 10^{19}$ at cm^{-3}) under the same maximum load (10 mN). Two different diffraction conditions were used. For all indentation loads, a dense and isotropic area was detected around the indent site while rosette arms extend further along $\langle 110 \rangle$ directions parallel to the surface.

The central zone corresponds to a highly strained zone where it is very difficult to recognize any individual dislocation. The presence of huge plastic strains (ϵ_z reaches values as high as 28% just beneath the indent site [14]) explains why it is so difficult to detect individual dislocations at the centre of the plastic zone. If we neglect the tip rounding of the indenter (imperfect shape) geometrical similarity suggests that the same strain values are obtained whatever the load, only the plastically deformed volume changes. As discussed in section 2, the size of this dense and central zone increases linearly with the square root of maximum load applied on the indenter and this dependence allows determining the flow stress of the sample.

Under the highest loads an asymmetrical rosette appears due to the geometry of the used tip. We employed a Berkovich tip that is three-sided with one flank set normal to one $\langle 110 \rangle$ rosette arm direction. Along the direction normal to the indenter flank, only one arm forms (on the flank side) while two arms form on both sides of the indenter along the orthogonal direction. These results reveal that indenter orientation, or say flank inclination relative to slip planes, rules whether one or two arms form along a $\langle 110 \rangle$ direction.

Most perfect dislocation lines constituting a rosette arm along the $[110]$ direction (resp. $[-110]$) were observed to vanish under a $g = -220$ diffraction condition (resp. 220). Therefore, their Burgers vector is determined to be parallel to arm direction $b = a/2 \langle 110 \rangle$. In the n-doped specimens, the dislocation lines are formed by long segments parallel to the arm direction and are the screw parts of the dislocation loops. P-doped samples, in contrast, showed very few screw segments either in the symmetrical or asymmetrical arms. Following the model of Warren et al. [18], 60° segments are of $\alpha = [B]g$ type in the rosette arms developing along the $[110]$ direction and of $\beta = [A]g$ type along the orthogonal direction. The differences in the dislocation shape observed between the n- and p-doped specimens suggest that the screw segments develop less rapidly in the n-doped specimens and are still present in these foils, while screw segments having larger mobility in the p-doped specimens develop in depth outside the selected superficial zone used for TEM observations (foils were prepared from the undeformed side). The proposed dislocation arrangement is shown schematically in Fig. 5. It is to be noted that Yonenaga's velocity measurements are available at elevated temperatures and low stresses only [19]. So far, these actually reveal strong differences between n- and p-doped specimens indicating lower dislocations mobilities in the n-doped ones, in particular, for screw segments supporting the proposed model.

An important feature of the rosette arms is the presence of partial dislocations and extended stacking faults that were found at the indented surface. These are easily detected in a TEM using a diffraction condition that sets, in contrast, the associated stacking faults. Again doping of the samples appears to play an important role. In fact, while stacking faults are obvious in the n-doped specimens they are not detected in the p-doped specimens (under the range of loads used here). Another striking feature is that in the n-doped specimens, we could detect stacking faults in both rosette arms. The presence of microtwins has been reported extensively under microindentations [4-9] and also detected at nanoindentations [10, 11]. Until recently [4], it has been considered that GaAs, contrary to other III-V semiconductors, showed stacking faults in only one rosette arm. This striking behaviour was not well under-

stood. Moreover, the character of these microtwins was controversial. We reveal here that, first, stacking fault presence depends on doping and, second, they may appear in both rosette arms instead of only in one of them.

Recently, Wang et al. argued that microtwins were associated to cracks. When perfect dislocations could be emitted, they accommodated the indentation stresses and, hence, avoided fracture. In the nanoindentation regime, no cracks are formed, so far microtwins are emitted in n doped specimens in both rosette arms, while in agreement with the suggestions of Wang et al. [4] they do not exist in p doped ones. This suggests that doping plays an important role here.

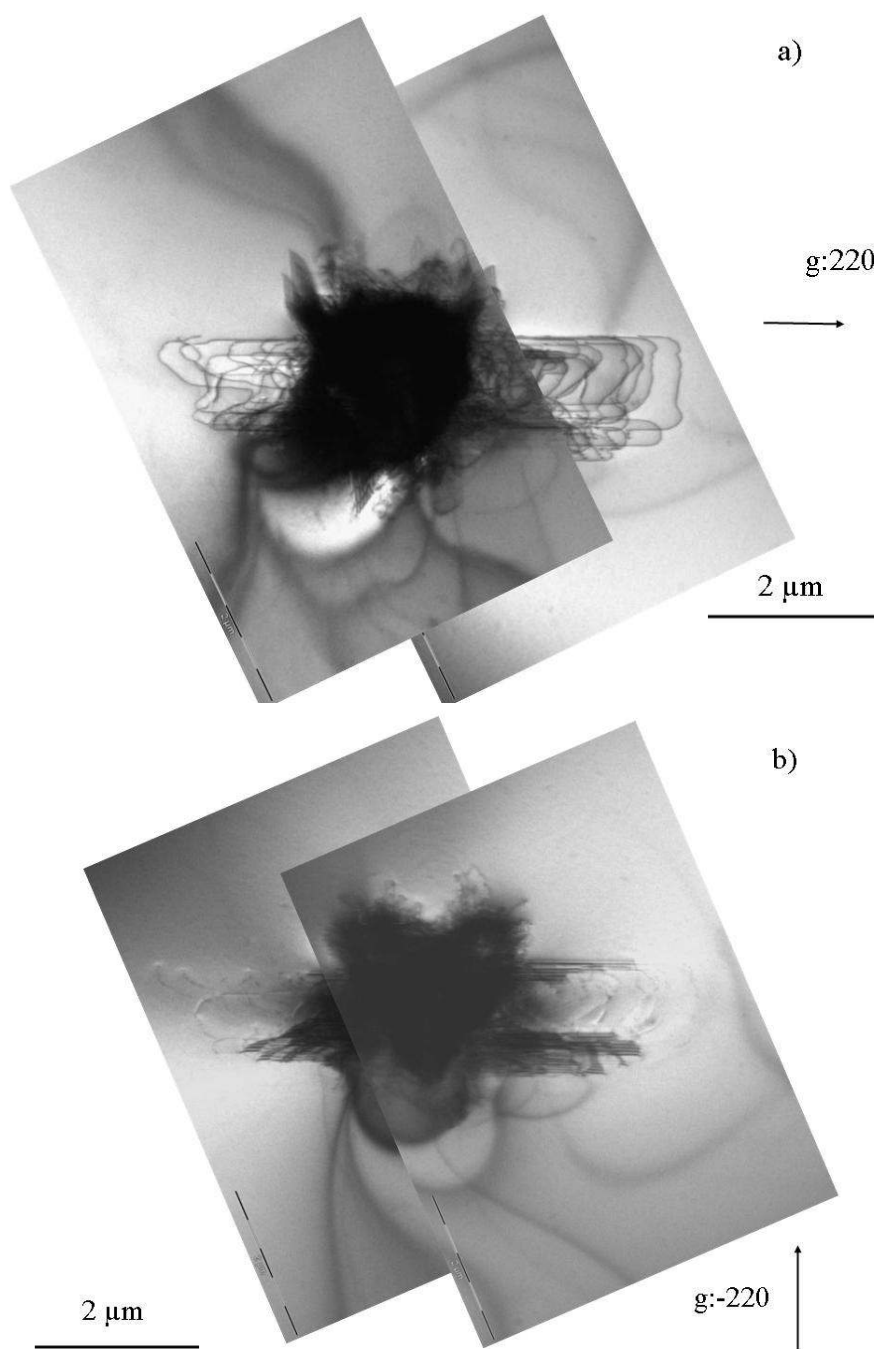


Fig. 3. TEM plan view images of indent site made in n-doped GaAs under 10 mN at RT: a) $g = 220$ diffraction condition; b) $g = -220$ diffraction condition.

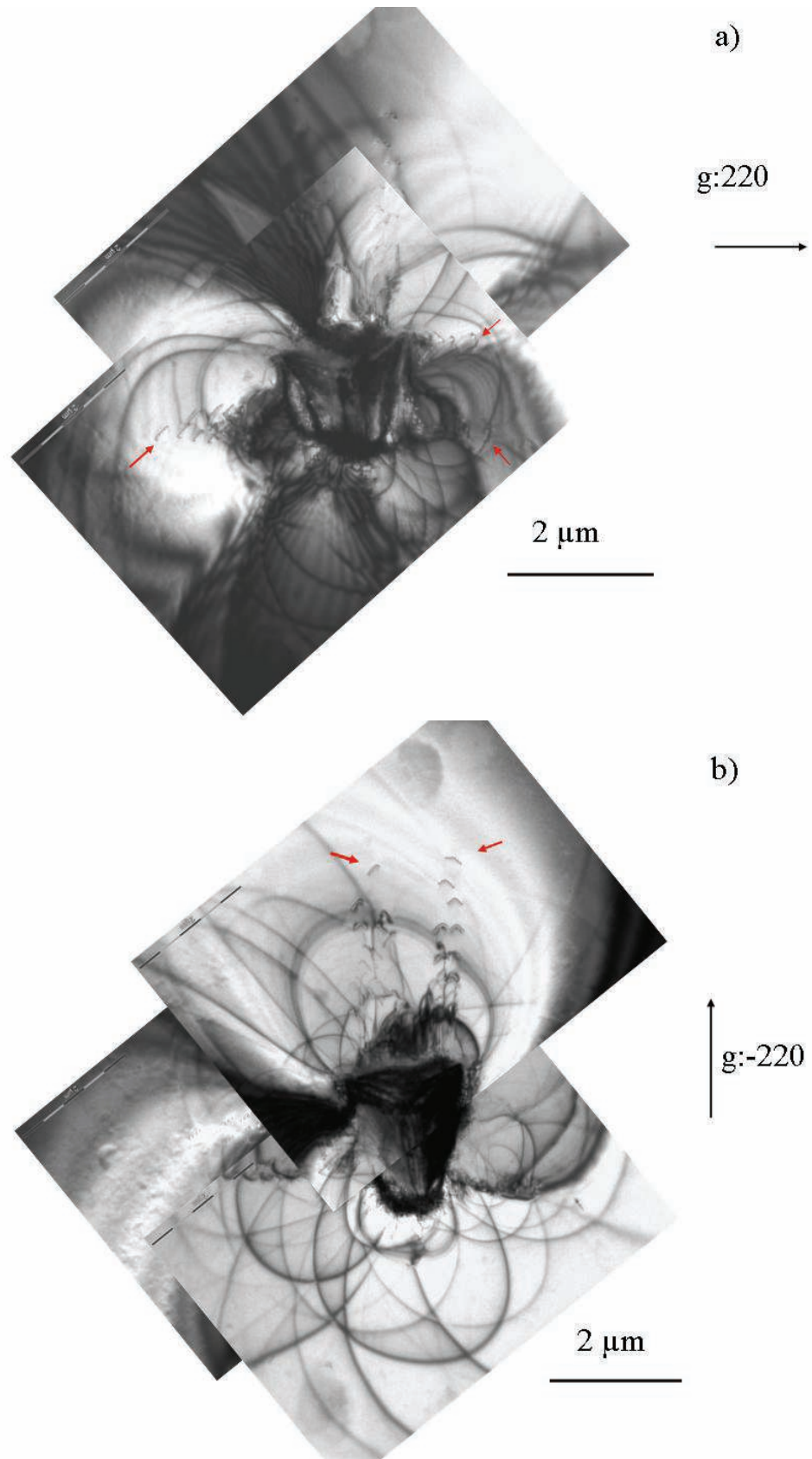


Fig. 4. TEM plan view images of indent site made in p-doped GaAs under 10 mN at RT: a) $g = 220$ diffraction condition; b) $g = -220$ diffraction condition.

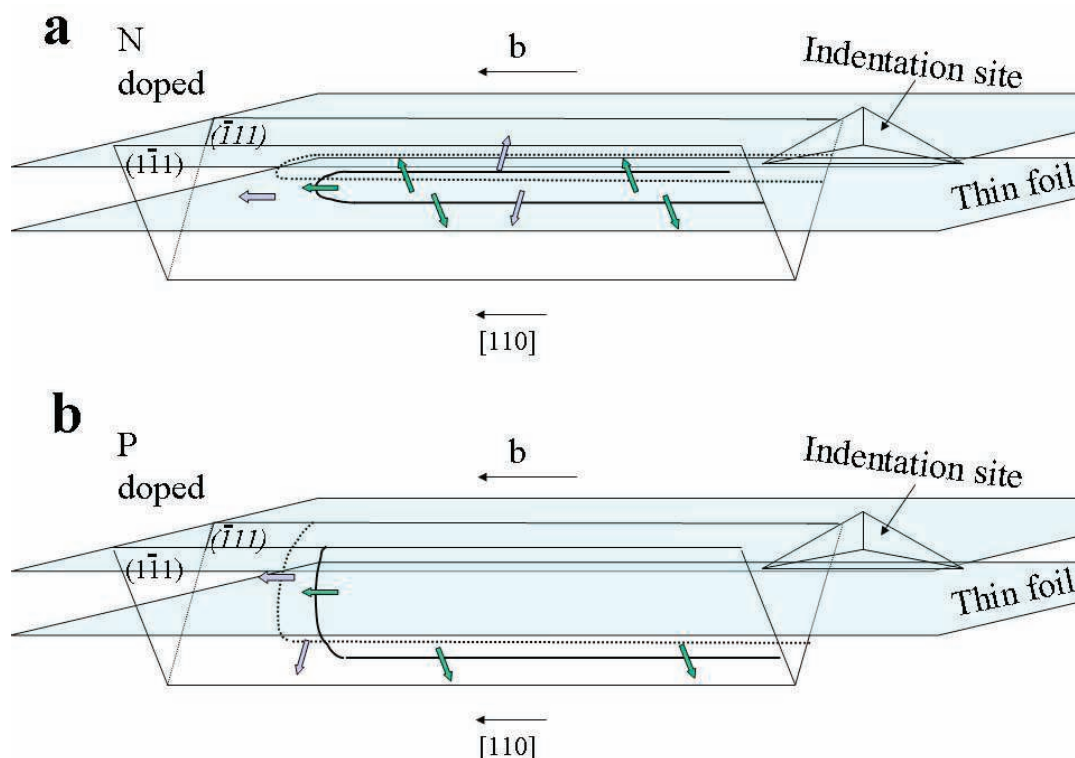


Fig. 5. Rosette arm schematics for n-doped (a) and p-doped (b) specimens based on screw segment velocity difference with 60° ones. We suppose that in n-doped specimens the screw segments propagate much slower than 60° ones and are observed in the TEM foil, while they escape the thin foil volume in p-doped specimens.

Large widening of stacking faults has been attributed to lower frictional force on the leading partial [20, 21], the dislocations most commonly observed being those moving with the lowest mobility (30° partials, the character of the leading partial changing from 90° to 30° as the loop expands) [22, 23]. Our results suggest that difference in mobility between leading and trailing partials would be less important in p-doped specimens. There is indeed experimental evidence showing that the difference in the mobilities of dislocations is smaller in Zn(p) doped GaAs crystals [19, 21, 24]. The contribution of the free surface could also be considered in the proposed mechanism since microtwins are observed at the surface systematically. Dislocation separation could be facilitated at the emergence at the surface. Repeating the mechanism of SF extension on adjacent $\{111\}$ planes results in the twinning of the crystal. Some authors have argued that SF energy of (111) and $(\bar{1}\bar{1}\bar{1})$ was lower than that of $(\bar{1}11)$ and $(1\bar{1}\bar{1})$ planes due to anisotropy [5, 25]. This explanation was clearly not satisfactory since we show in the elastic-plastic domain that anisotropy is much less important.

4. Geometrical size effect

Contact mechanics has been developed for semi-infinite half space [13], this assumption being not fulfilled when the size of the plastic zone becomes of the order of one of the object dimensions and then size effects are expected [26-28]. For instance, thin structures are expected to show a mechanical behaviour quite different from that of a bulk. Recent studies in the field of semiconductors showed that indeed when the contact depth to thickness ratio h_c/t approaches 3%, a free standing film cannot be considered as a semi-infinite half space any-

more and plastic deformation of the free bottom side should be taken into account [27]. These length-scale effects may have important implication in the growing of mismatched layers for optoelectronic devices [2]. Thin walls can be formed by photolithography on top of GaAs substrate to induce plastic compliance which can be tailored by adjusting the aspect ratio (height $\bar{h}$ and width w , Fig. 6). Indeed, dramatic differences in the indentation response are observed. When the test is carried out on thinner and/or higher walls, the loading-unloading curves are shifted to the right-hand side of the figure (larger penetrations), which means that the total penetration of the indenter at a given load depends on type of wall (Fig. 6).

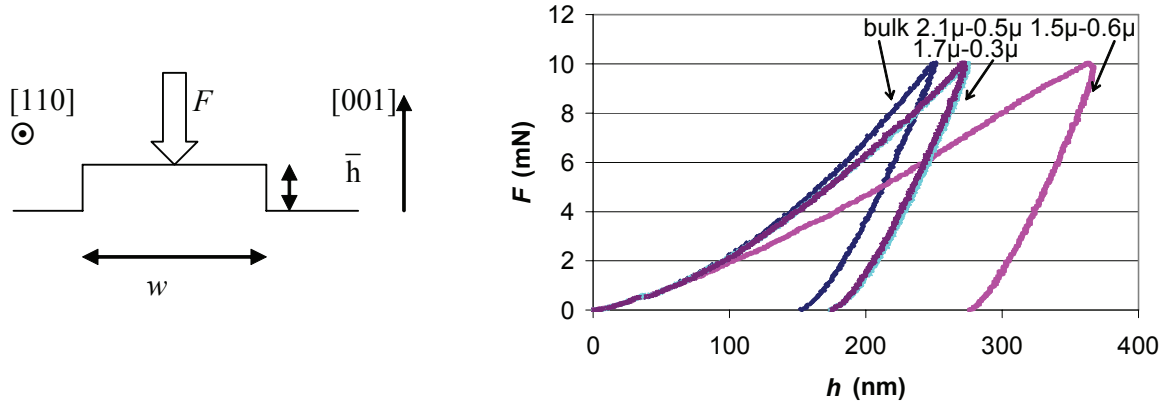


Fig. 6. Geometric (shape) characteristics and orientation of the tested GaAs thin walls. Load F is applied with the tip approximately positioned at the wall centre (left). Load-penetration curves obtained for different wall geometry (width w - height $\bar{h}$, for a bulk $w = \infty$ and $h = 0$) with indenter tip located at the wall centre (right).

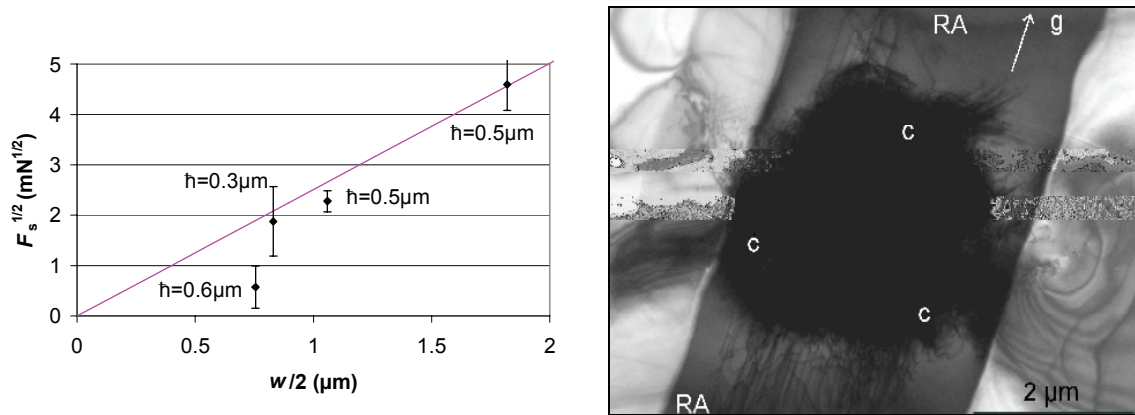


Fig. 7. Load at separation F_s from the bulk response (load applied to wall centre). The line corresponds to that calculated from Eq. 4 (left). TEM plan view (right) of a $3.6\mu\text{m}-0.5\mu\text{m}$ wall indented under 20 mN (with indenter tip approximately located at the wall centre, $g = 220$, RA for rosette arms, c for central plastic zone).

While all loading curves superimpose under low loads they eventually separate from that of the bulk at loads F_s that appear to depend on type of wall. After separation, the total penetration is determined to be more important when a wall is tested as compared to the bulk reference. The ‘flat’ surface (bulk substrate) shows minimum deformation while the thinner and higher wall shows maximum deformation. Intermediate behaviour is observed between these two extremes. It should be noted that the intermediate curves ($2.1\mu\text{m}-0.5\mu\text{m}$ and $1.7\mu\text{m}-0.3\mu\text{m}$ specimens) almost overlap. It can be anticipated in view of these curves that the apparent ‘hardness’ of the wall depends on its geometric characteristics and that height and width play reverse role. Let us consider the load F_s at

which the loading curves obtained for a given wall separate from that of the bulk taken as a reference. The square root of the respective loads is shown in Fig. 7 as a function of half of the width $w/2$ of the considered wall. As expected from Fig. 6, the thinner and higher wall shows deviation at the smallest load while intermediate situations are observed for the other walls.

Figure 7 shows a plan-view TEM micrograph of an indent site in a $3.6\mu\text{--}0.5\mu$ wall under 20 mN when the tip is approximately positioned at the centre of it. The plastic zone is composed of a central and dense region and rosette arms which extend along the $\langle 110 \rangle$ directions parallel to the indented surface. The extension of the central plastic zone can be predicted in a bulk specimen by Eq. (3) and using for GaAs a flow-stress value about $Y_R = 3$ GPa. Under a 20 mN load it is in fact expected to be about $c = 1.8 \mu\text{m}$ (in the bulk). Actually, the central plastic zone is fully contained into the wall (Fig. 7). The rosette arms parallel to the wall along the $[110]$ direction are observed to extend at distances of about $4 \mu\text{m}$. They are formed by individual dislocations which generally look like half hairpins with a long screw segment. In contrast, the rosette arms extending normally to the wall sides are truncated. It should be noted that deviation of the mechanical response of the $3.6\mu\text{--}0.5\mu$ wall from the bulk response is detected in a range of 16-25 mN loads when rosette arms already reach the wall sides. Hence, TEM offers important insight into wall response since, suggesting that indentation response is predominantly ruled by the development of the central-plastic zone. Equation (3) can be inverted into

$$\sqrt{F_s} = \sqrt{\frac{2\pi Y_R}{3} c} = \sqrt{\frac{2\pi Y_R}{3} \frac{w}{2}}, \quad (4)$$

where F_s is the load required to generate into a bulk specimen of a central plastic zone with a radius equal to one-half of the wall width; $c = w/2$. F_s as a function of $w/2$ is shown in Fig. 7 as a continuous line for GaAs using a flow stress Y_R value about 3 GPa. Equation (4) yields a relatively good estimation of the load at separation. Note that Eq. 4 does not take into account the height of the wall while this parameter clearly influences the behaviour, as said before. A complete understanding of the wall behaviour requires the aspect ratio h/w to be considered [29]. Nevertheless, Fig. 7 suggests that deviation criterion can be formulated as follows: deviation in indentation response happens at loads corresponding to central-plastic-zone extension (in the bulk substrate) that reaches one-half of the wall width. This simple criterion means that deviation is obtained when the central-plastic zone extends to the wall side. By the way, rosette arms propagating normally to the wall side already emerged.

It should be noted that rosette arms correspond to the gliding of only a few dislocations as compared to the elevated density of dislocations in the central zone (Fig. 7). A simple estimation of the number of dislocations generated by the indenter is $n = h_r/b_z$, where h_r is the residual depth of the indent and b_z is the Burgers-vector component of the dislocations along the loading axis. Taking $h_r \sim 235$ nm, one finds $n \sim 800$ dislocations generated by the indenter under the present experimental conditions (maximum load $F_m = 20$ mN), while rosette arms contain about 30 individual dislocations (Fig. 7). The present result emphasizes the predominant role played in the mechanical response by the central-plastic zone over the rosette arms.

5. Conclusions

Instrumented nanoindentation allows extracting the mechanical behaviour of small volumes that scale with those encountered in semiconductor devices. It allows for deep insight into the plastic behaviour of semiconducting structures. So far, further development should consider temperature influence since devices follow complex thermomechanical routes. We have illustrated that TEM is an utmost complementary tool to study local plasticity. Instrumented nanoindentation associated to TEM will allow for further understanding of plastic deformations in such structures and will open practical routes to improve the devices.

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References

- [1] A. George and J. Rabier, *Rev. Phys. Appl.*, 22, 941, (1987).
- [2] G. Patriarche and E. Le Bourhis, *J. Electronic Mater.* 32, 861, (2003).
- [3] T. Suzuki and T. Ohmura, *Phil. Mag. A*, 74, 1073, (1996).
- [4] S. Wang and P. Pirouz, *Acta Mater.*, 55, 5526, (2007).
- [5] H.R. Höche and J. Schreiber, *J. Phys. Stat. Sol. (a)*, 86, 229, (1984).
- [6] A. Lefebvre, A. Androussi, and G. Vanderschaeve, *Phys. Stat. Sol. (a)*, 99, 405, (1987).
- [7] C. Levade and G. Vanderschaeve, *Phys. Stat. Sol. (a)*, 171, 83, (1999).
- [8] S. Koubaïti, C. Levade, J.J. Couderc, and G. Vanderschaeve, *Eur. Phys. J. Appl. Phys.*, 1, 141, (1998).
- [9] D. Grabco, O. Shikimaka, and E. Harea, *J. Phys D: Appl. Phys.*, 41, 074016, (2008).
- [10] E. Le Bourhis and G. Patriarche, *Phil. Mag. Lett.*, 79, 805, (1999).
- [11] L. Largeau, G. Patriarche, F. Glas, and E. Le Bourhis, *J. Appl. Phys.*, 95, 3984, (2004).
- [12] D. Tabor, *Phil. Mag A*, 74, 1207, (1996).
- [13] K.L. Johnson, *Contact Mechanics*, Cambridge University Press, 171-179, 1985.
- [14] L. Largeau, G. Patriarche, and E. Le Bourhis, *J. Mater. Sci. Lett.*, 21, 401, (2002).
- [15] E. Le Bourhis, *Glass mechanics and technology*, Wiley VCH, Weinheim, 291-309, 2008.
- [16] E.T. Lilleodden, W. Bonin, J. Nelson, J.T. Wyrobek, and W.W. Gerberich, *J. Mater. Res.*, 10, 2162, (1995).
- [17] D. Kramer, H. Huang, M. Kriese et al., *Acta Mater.*, 47, 333, (1999).
- [18] P.D. Warren, P. Pirouz, and S.G. Roberts, *Phil. Mag. A*, 50, L23, (1984).
- [19] I. Yonenaga, *J. Phys.*, III, 7, 1435, (1997).
- [20] P. Pirouz, *Scripta Met.*, 21, 1463, (1987).
- [21] G. Vanderschaeve, *Solid State Phenomena*, 59-60, 145, (1998).
- [22] A. Lefebvre and G. Vanderschaeve, *Phys. Stat. Sol. (a)*, 107, 647, (1988).
- [23] A. Lefebvre, Y. Androussi, and G. Vanderschaeve, *Phil. Mag.*, 56, 135, (1987).
- [24] T. Ninomiya, *J. Phys. Colloques*, 40, C6, (1979).
- [25] M.R. Suroviec and B.K. Tanner, *J. Appl. Cryst.*, 20, 499, (1987).
- [26] Y. Choi and S. Suresh, *Scripta Mater.*, 48, 249, (2003).
- [27] L. Largeau, G. Patriarche, A. Rivière, J.P. Rivière, and E. Le Bourhis, *J. Mater. Sci.*, 39, 943, (2004).
- [28] J. Michler, K. Wasmer, S. Meier, F. Östlund, and K. Leifer, *Appl. Phys. Lett.*, 90, 043123, (2007).
- [29] E. Le Bourhis and G. Patriarche, *Acta Mater.*, 53, 1907, (2005).