Effect of electronic doping on the plasticity of homoepitaxial 4H-SiC single crystals

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Abstract. Instrumented micro-indentations have been performed at room temperature on 4H-SiC homoepitaxial single crystals with different doping. For these experiments, it appears that the pop-in event occurs at the same level of load for intrinsic and n-type SiC and at a higher load level for p-type. Correlation of the pop-in event with dislocation nucleation indicates that doping acts on dislocation nucleation and that p-type doping plays a hardening role on the plastic behaviour of 4H-SiC. This result is confirmed by the conventional measurement of imprint size using scanning electron microscopy.

1. Introduction
It is well known that impurities play an important role in plasticity of materials. They usually act as obstacles to dislocation propagation through direct interaction with dislocations. This metallurgical effect requires generally a noticeable concentration of impurity to be evidenced. However, impurities play also a remarkable role in the plasticity of semiconductors at concentrations much lower than 1%. In this case, doping does not act through direct interaction with dislocations but through electronic effects. Such effects have been put in evidence in several semiconductors. Silicon is the one in which the effect has been observed and the most studied, by direct measurements of dislocation velocity [1], as well as by measurements of the lower yield stress [2] or extension of rosette arms after indentation [3]. As a consequence, electronic doping yields a modification of the Brittle-to-Ductile Transition Temperature ($T_{BDT}$). It is expected that due to the wide band-gap of SiC (3.2 eV for the 4H-polytype) doping could significantly modify $T_{BDT}$ in this material. However this has not been evidenced yet, although silicon carbide has both important mechanical and electronic applications.

In this paper, some results of microindentations performed at room temperature on intrinsic, n-type and p-type 4H-SiC homoepitaxial layers are presented. Results are compared with the literature for other semiconductors and discussed in the framework of the plasticity of these materials.

2. Experimental
Materials used in this study have been supplied by LETI (CEA-Grenoble, France) and were grown by the Lely method. A 10µm thick layer of different doping intrinsic ($N_i \sim 6 \times 10^{13}$ cm$^{-3}$), n-type ($N_n \sim 8 \times 10^{17}$ N atoms cm$^{-3}$) and p-type ($N_p \sim 4 \times 10^{17}$ Al atoms cm$^{-3}$) was homo-epitaxied at 1550°C on a
4H-SiC substrate oriented 7° off the basal plane. Microindentations using a Fischerscope H100CXYp equipped with a Vickers indenter were performed at room temperature on the (0001) Si-surface up to maximum loads of 50 mN and 300 mN. The maximum load was reached within 20 seconds and dwelt for 5 s. An array of fifty indentations was made on each sample (figure 1). The indentation diagonals were oriented to be parallel to <1120> and <1100> directions (figure 2) determined from back reflection X-ray Laue patterns taken prior to the tests. Scanning Electron microscopy (SEM) was used to measure the size of imprints.

![Figure 1](image1.png)  
**Figure 1.** Optical microscopy of a typical array of indentations made on a homoepitaxial layer under a load of 300 mN.

![Figure 2](image2.png)  
**Figure 2.** Micrograph of an imprint observed by SEM. Diagonals are along <1100> and <1120> directions.

### 3. Results

Typical curves under a maximum load of 50 mN obtained on different doped layers are shown in figure 3. The maximum penetration depth is lower than 0.3 µm, which is much smaller than the thickness of the layer. Under these conditions, the influence of the substrate can be neglected and the recorded curves are representative of the behaviour of the material of the layers. A well-defined pop-in event, i.e. a sudden penetration of the indenter at constant load, is observed on each curve. The pop-in is usually associated to the onset of plasticity: the first irreversible events occur at this point, and are usually assumed to correspond to the nucleation of dislocations. The level of pop-in occurs at the same load for intrinsic and n-type material. For the p-type layer, pop-in occurs at a higher load. A statistical analysis has been made from the fifty imprints on each sample. This leads to pop-in levels of $4.7 \pm 0.6$ mN, $4.2 \pm 0.5$ mN and $7.9 \pm 1.6$ mN, for n-type, intrinsic and p-type material, respectively. Unfortunately, from these values it is not possible to get the actual stresses responsible of pop-in events because the actual stress field beneath a Vickers indenter is difficult to sort out. Nevertheless, the link between the pop-in event and the dislocation nucleation indicates that nucleation of dislocations is more difficult when material is p-type doped as compared to intrinsic or n-type doped material.

From the unloading part of the load-penetration curve, a hardness value can be extracted providing that the response of the material during unloading is elastic and the contact surface beneath indenter remains constant. The systematic observation of cracks at the ends of imprints (see figure 2) does not allow such a hypothesis to be valid. This is why we used the classical way to get the hardness value, i.e. by measuring *post-mortem* by SEM the size of the diagonals of the imprints, as it is usually done for bulk materials under high loads. From measurements of imprint size made under a load of 300 mN on intrinsic and p-type (no measurements have been performed on n-type) we obtained Vickers hardness values of $32.6 \pm 0.2$ GPa and $33.8 \pm 1.2$ GPa, respectively. Whatever the quite poor accuracy of the hardness value for p-type material, these results are in accordance with the pop-in levels. It can be claimed that p-type doping has a hardening effect on the plasticity of 4H-SiC.
Figure 3. Typical load-penetration depth curves for (a) intrinsic, (b) n-type and (c) p-type 4H-SiC. Pop-in is observed for the three materials. A magnification of the pop-in region is given on each curve. (d) Pop-in level and area of load-penetration curve as a function of doping.

A value of the dissipated energy during the loading-unloading experiment is given by the area of the load-penetration curve. It is assumed that this value gives a good description of the resistance of materials to indentation [4]. The results are presented in figure 3 (d) from experiments made up to the maximum load of 300 mN. The energy dissipated by plasticity and/or fracture is found to be lower in p-type. Qualitatively, this is in accordance with Vickers hardness values and pop-in levels.

4. Discussion

Many studies by micro- and nano-indentation have been conducted in semiconductors, some of them being dedicated to the influence of doping. In the case of silicon, analysis of nanoindentation tests suffers from phase transformations occurring beneath the indenter. Multiple pop-ins and pop-outs have been reported; the cause of pop-ins is not clear at this time, but the pop-outs are assumed to be due to phase transformations [5, 6]. The phase transformations disappear and the sample deforms by classical dislocation plasticity when the sample becomes thin and comparable in width to the size of the nanoindenter, however the influence of doping has not yet been checked in these conditions [7]. Following other authors, pop-in events could be the signature of subsurface cracking or sudden dislocation bursts [8]. Le Bourhis and Patriarche have analyzed the structure of nanoindentations in heavily n- and p-doped GaAs. This material does not suffer phase transformation, and the authors observed that the mechanical response of both types of samples is relatively similar with a level of pop-in which is not affected by doping [9]. In contrast, the indentation rosette structure is different. Perfect dislocations with long screw segments emanate from imprints in n-doped specimens, as well as partial dislocations on both arms of rosettes, whereas p-type specimens show no partial dislocations. From these results, the different behaviour as a function of doping could be related to a difference in mobility of dislocations. This is in accordance with the huge effect of doping observed by plastic deformation under pressure in bulk GaAs [10].

Contrary to silicon and similar to GaAs, it has been shown that the plasticity response of SiC to nanoindentation occurs by dislocation plasticity rather than by densification or phase transformation.
The first indirect evidence of such a behaviour was the observation of the pop-in phenomena in 6H-SiC [11]: TEM observations have demonstrated that dislocations are emitted from imprints and lie in the basal plane, but no precise analysis of dislocations (perfect or partials) was performed [12]. By compression of bulk material [13] and classical indention tests [14] as a function of temperature, a high asymmetry in mobility of partial dislocations has been shown, which is important in that the temperature is low. Unfortunately, all experiments reported above were conducted on as-grown crystals in which doping level was not controlled during the elaboration process; however all silicon carbide samples used had a high content of N atoms. From the results presented in this paper, it appears that doping modifies the mechanical response of 4H-SiC. P-type doping leads to a higher level of pop-in as compared to intrinsic material whereas n-type has no significant effect. Considering that pop-in is related to nucleation of dislocations, our results show that this phenomenon is strongly affected by p-doping, making it more difficult. As a matter of fact it is the first time that the level of pop-in can be related to the doping effect in a semiconductor allowing it to be shown that nucleation of dislocations can be affected by electronic doping as was shown for dislocation velocity. However in this context a point to be questioned is the actual site of dislocation nucleation. The basal plane is the easy glide plane for hexagonal silicon carbide, but from a geometrical point of view, dislocations should be nucleated on other planes to accommodate deformation due to an imprint on the basal plane. A few papers in the past have mentioned the activity of prismatic planes [15, 16]. By indentation on a prismatic plane, Mussi et al. [16] have observed short segments of dislocations on other prismatic planes. Those dislocations are perfect dislocations but they cross-slip in the basal plane where they dissociate, indicating the possibility of dislocations to be nucleated on such planes. TEM observations on homoepitaxial layers of different doping have to be done to check dislocation nucleation sites. Moreover, nanoindentation using a spherical indenter would give access to the actual stress corresponding to pop-in events and to dislocation nucleation stress. This work is in progress.

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