Nanoindentation of semiconductors: experiment and atomistic simulations

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Abstract. With recent developments in advanced materials and nanostructures, particularly those designed for electronics, it is evident that their successful application will depend not only on their electrical properties, but also on their mechanical characteristics. Nanoindentation is a unique method for examining nanostructured materials, as it requires a small volume of the solid and probes the surface layers of particular interest. Nanoindentation of bulk semiconductor crystal structure has been frequently used to study the onset of irreversible deformation - incipient plasticity. Here we present recent experiments supported by molecular dynamics simulations that allow determination of the origin of incipient plasticity in GaAs crystals. It will be demonstrated that, as in case of silicon, plastic deformation of GaAs starts from a pressure-induced structural phase transformation.

1. Introduction

There has been significant recent progress in our understanding of incipient plasticity, coming from nanoindentation experiments \cite{1} supported by atomistic simulations \cite{2}. The onset of plasticity is usually marked by characteristic singularities on indentation load-displacement (\(P-h\)) curves. There are so called “pop-in events”, where indenter suddenly penetrates material at the constant load. Results of nanoindentation experiments by Corcoran \textit{et al} \cite{3} and Gouldstone \textit{et al} \cite{4} indicate that the pop-in events in metals are caused by homogeneous dislocations nucleation under the indenter tip. This view has recently been completed due to high temperature nanoindentation experiments \cite{1} that linked the onset of plasticity in metals with heterogeneous nucleation of dislocations at preexisting vacancy clusters.

Semiconductors subjected to the stress caused by the indenter develop deformation through dislocation nucleation or/and the structural phase transformation. This issue comes to light during nanoindentation of silicon crystals. Indeed, the loaded Si-I (cubic diamond - \(cd\)) structure gradually transforms to metallic Si-II (\(\beta\)-tin) when the pressure of \(-11\) GPa is attained under the indenter tip. The \textit{in-situ} conductivity measurements combined with nanoindentation experiments \cite{5} reveal that plastic deformation in silicon is initiated by the phase transformation, while the dislocation activity takes place within previously nucleated Si-II phase \cite{6}. During unloading one observes the set of phase transformations that include transition to a mixture of cubic Si-III (bc8) and its rhombohedral...
modification Si-XII (r8) phases or to amorphous silicon (a-Si) [6]. The transformation to Si-III/Si-XII phase is discontinuous resulting in discrete “pop-out event”, while transformation to amorphous modification of silicon is gradual and is evidenced by “elbow” on unloading part of P-h curve.

In contrast to silicon, for which the origin of incipient plasticity is resolved, the case of GaAs is under continuing debate. Nanoindentation experiments exhibit the pop-in event (the end of elastic deformation) during loading and no singularities during unloading of GaAs crystals [7]. The fact that dislocations and slip traces can be found in cross-sectional TEM observations of residual impressions accompanied by an absence of any trace of non-zinc-blende phase of GaAs made the previous authors to attribute the onset of plastic deformation dislocations nucleation [8]. This hypothesis was supported by continuum theory of dislocations that predicts the theoretical shear stress (τc) for homogeneous dislocation nucleation to be a tenth of the shear modulus (G). The maximum shear stress can be calculated from the formula

\[ \tau_c = 0.465 \frac{p_m}{\mu} \]

where \( p_m \) is the mean contact pressure. Measurements by Bradby et al [10] demonstrated that the mean contact pressure at the pop-in events are sufficient to initiate homogeneous dislocation nucleation reaching approximately 11 GPa. On the other hand, Benson et al [11] reported that the zinc-blende-to-orthorhombic transition of GaAs starts at 12.5 ± 1.5 GPa and ends at pressure of 17.5 GPa. Therefore, the phase transition based explanation of the incipient plasticity in GaAs should be carefully verified.

The present review addresses the nanoindentation experiments accompanied by simultaneous conductivity measurements used to study the onset of plastic deformation in GaAs [12]. We demonstrated that zinc-blende phase of GaAs (GaAs-I) undergoes metalization and subsequent transformation to orthorhombic rocksalt-like structure (GaAs-II) during loading part of nanoindentation. Phase transformation occurs at the instant of pop-in event being the origin of the GaAs incipient plasticity.

2. Methods

Two 1µm epitaxial GaAs layers with varying Si dopant concentrations were grown by molecular beam epitaxy (MBE) on 350 µm thick GaAs (100) epi-ready substrates. The doping levels of the MBE-grown GaAs layers were \( N_{Si} = 10^{16} \text{ cm}^{-3} \), and \( 10^{18} \text{ cm}^{-3} \). Their electro-mechanical properties were studied by nanoindentation coupled with conductivity measurements [12]. Conclusions derived from nanoindentation experiments were supported by theoretical consideration based on molecular dynamics [13] and first-principle calculations [12].

2.1. Nanoelectrical measurements

In order to study the structural changes in GaAs during nanoscale deformation, we used a conductive nanoindentation system with a conductive boron-doped (\( N_d = 10^{21} \text{ cm}^{-3} \)) diamond indenter and voltage source (V) to obtain a time correlation of force, displacement, and electric current. The constant voltage is applied to the sample while the magnitude of current running through the tip/sample contact was monitored. The noise floor of the system is below 10 pA, allowing the investigation of pressure-induced microstructural changes.

The nanoindentations were carried out with increasing load over a 20 s period then holding at the maximum load for 10 seconds and finally gradual unloading over 20 s while applying a reverse bias of 3V. The majority of nanoindentations was performed with maximum load of 8 mN.

2.2. First-principle calculations

To study the equilibrium and contact properties of GaAs zinc-blende and rocksalt structures density functional theory (DFT) based calculations were carried out employing the QuantumEspresso code [14]. A pseudopotential method was applied within a local density approximation (LDA) using Perdew-Zunger parametrization of the exchange and correlation functional. The calculations used a supercell based on the face-centered cubic structure and filled with 48 Ga and As atoms, forming 24 consecutive (100) layers of zinc-blende and the subsequent rocksalt phase. The supercell was relaxed...
along the z-axis and the selfconsistent DFT calculations were applied to relax the structure. The convergence of the total ground state energy was found with plane wave-energy cutoff of 30 Ry and 8x8x2 Monkhorst-Pack mesh in the \(k\)-point space. The equilibrium properties of zinc-blende and rocksalt phases of GaAs were investigated by calculating their total ground state energy versus unit cell volume curves and subsequently searching common tangent slope that marks equilibrium hydrostatic pressure.

2.3. Molecular dynamics
In order to simulate nanoindentation deformation of the GaAs crystal the molecular dynamics (MD) code PARCAS by Nordlund et al [15] was used. The interactions between GaAs set of atoms were modeled by three-body Tersoff type potential [16] developed to be able describe both the zinc-blende and rocksalt phases of GaAs. The validity of the selected three-body potential was confirmed by calculations of the many physical properties of both considered structures. The interaction between carbon atoms of cubic diamond structure of indenter with GaAs was realized with Ziegler-Biersack-Littmark purely repulsive potential [17].

MD simulations were restricted to the cuboidal cell (size of 316x316x158 Å\(^3\)) formed by zinc-blende structure (a=5.635 Å). Four bottom GaAs layers were immobilized while the upper (001) plane was indented by diamond (a=3.567 Å) cube (size of 28x28x28 Å\(^3\)). The time step of numerical integration of the equation of motion was established to be 0.6 fs assuring the algorithm stability. Each indentation step was composed of indenter shift along [001] direction and then structural relaxation over 20000 time steps.

![Figure 1](image_url). Complex electro-mechanical response to nanoindentation of the low-doped GaAs (a) and Si (b). The sudden current drop (“current spike”) recorded for GaAs marks the onset of plastic deformation.

3. Results and discussion
The typical electric response to nanoindentation of low-doped GaAs under reverse bias of 3 V is displayed in the figure 1a. Initially perfect Shottky barrier leaks during loading as a consequence of band gap decreasing with applied pressure [12]. Subsequently, the gradual increase of the current flow is halted when rectifying contact is restored. Sudden drop of the electric current at the moment mechanical pop-in shows the unique correlation between two different phenomena.

The \(I-h\) characteristic registered for low-doped GaAs sample were compared with that obtained for silicon (figure 1). While “current-spike” is observed for GaAs, the electrical response of silicon to nanoindentation is completely different exhibiting gradual increase of the electric current without any significant singularity (figure 1b). This result agrees with data collected from electrical measurements performed by Ruffell et al [5]. They reported similar \(I-h\) relationship for silicon proving that complex
contact composed of metallic indenter and Si-II phase under the tip surrounded by Si-I phase has Ohmic character.

Figure 2. I-V characteristics collected for GaAs samples at load of 1 mN (after pop-in) prove that physical phenomenon responsible for pop-in event simultaneously restores Schottky barrier halting the current flow in the system.

The conducting indenter in contact with GaAs surface produces Schottky barrier as seen from I-V characteristics (figure 2) collected at load 1 mN (after the pop-in). The applied reverse bias (positive voltage) halts current flow through the contact for the variously doped GaAs specimens. However, the junction with silicon concentration of $N_{Si}=10^{18}$ cm$^{-3}$ leaks for reverse bias exceeding ~3.5 V. The recorded effect agrees with common expectations based on classical theory of metal-semiconductor junction [18].

Figure 3. Nanoindentation of low-doped GaAs with maximum load of 220 $\mu$N. (a) The $P$-$h$ curve used for evaluation of the indenter tip radius. (b) Detailed observation of the correlation between electric “current spike” and mechanical pop-in event. The current is halted exactly at the moment of pop-in.

The detailed investigation of correlation between “current-spike” phenomenon and pop-in event was accomplished using lower maximum load of 220 $\mu$N sufficient to initiate plastic deformation in low-doped GaAs crystal (figure 3a). The initial elastic part of the $P$-$h$ relationship fulfills Hertz equation $P=(4/3)E\sqrt{R}h^{3/2}$ ($E$ – reduced Young’s modulus) that presents classical theory of elastic contact between the sphere of radius $R$ and isotropic half-space [19]. This made possible to estimate
the indenter tip radius to R=180 nm, a parameter necessary for mean contact pressure calculations. The pop-in event occurs at \( \sim 18 \) GPa while indenter penetration depth reaches the value of \( h=19 \) nm. Furthermore, the mean contact pressure release \( \Delta P_m=2.6 \) GPa is caused by pop-in. What comes as a revelation is that current increase initiated before the pop-in event drops down immediately at the instant of pop-in (figure 3b) i.e. the origin of GaAs incipient plasticity is also a cause of unexpected restoration of the perfect Shottky barrier.

The pop-in events were observed in almost all nanoindentations even though a few \( P-h \) curves without any singularities were recorded. It is explained [12] that the absence of pop-in event results in no current flow through the contact due to indentation in the certain place affected by preexisting dislocations. In this case the plastic deformation is expected to occur mainly by dislocation activity.

![Figure 4](attachment:image.png)

Figure 4. Influence of the silicon concentration on the mean contact pressure at the GaAs pop-in.

The decrease of the mean contact pressure at the pop-in caused by increased doping (figure 4) agrees with the DFT calculated decrease of the hydrostatic pressure at which GaAs-I and GaAs-II phases can exist in equilibrium (figure 5). This suggests a non-dislocation origin of the pop-in events, a conclusion supported by experiments showing that silicon doping of GaAs single crystals increase their critical resolved shear stress [20]. However, the influence of Si doping on the mechanical properties of GaAs is still unclear. Indeed, Yonenaga et al [21] showed that the critical stress for dislocation formation in silicon doped GaAs continuously decreases with temperature, being also greater than the critical stress measured for undoped GaAs. On the other hand, there are also literature reports showing that silicon doping makes GaAs softer at low temperatures [22,23].

In consequence, an explanation of the electro-mechanical coupling at pop-in can be derived from an assumption that the GaAs-I to GaAs-II phase transformation marks plastic deformation in GaAs. Findings by Benson et al [11] show that phase transformation from GaAs-I to GaAs-II starts at hydrostatic pressure of \( 12.5\pm1.5 \) GPa. The transition is continued until the pressure of \( \sim 18 \) GPa is reached. The rocksalt-like GaAs phase is thermodynamically unstable during pressure releasing and transforms into initial zinc-blende phase or composition of zinc-blende and amorphous phases depending on experimental conditions [11]. Comparison of the mean contact pressures achieved during our nanoindentations with pressure range of GaAs-I \( \rightarrow \) GaAs-II transition makes the phase transformation scenario a favorable explanation of the onset of gallium arsenide plastic deformation. Furthermore, Li et al [24] also considered the possibility of phase transformation during Vickers indentation of (110) surface of GaAs because of direct observation of amorphous phase in residual impression.

In order to support our main idea that the onset of plastic deformation (pop-in) in GaAs crystal is caused by GaAs-I \( \rightarrow \) GaAs-II phase transformation rather than dislocation nucleation we studied nanoindentation of GaAs by molecular dynamics simulations [13]. The interaction between the indenter and GaAs crystal revealed a singularity in the \( P-h \) curve corresponding to a pop-in event.
Analysis of the GaAs structure in the small volume right under the indenter showed a new peak at 90° angle while the prior-to-indentation peak at angle of 110° (characteristic for zinc-blende structure) completely disappeared. Confirmation of nanoindentation induced GaAs-I $\rightarrow$ GaAs-II phase transition comes from direct visualization of the transformed structure. The six-coordinated rocksalt-like phase was detected in the obtained visualization of the stressed GaAs structure simulated by MD method [13].

![Figure 5](image)

**Figure 5.** Results of the DFT calculations showing decrease of the equilibrium hydrostatic pressure of the GaAs zinc-blende/rocksalt phases due to silicon doping.

Further argument supporting phase transformation origin of GaAs incipient plasticity comes from first-principle calculations of energy bands in the vicinity of the interface between semiconducting zinc-blende and metallic rocksalt structures. The calculated spacial distribution of energy levels exhibit band bending characteristic for Shottky barrier of metal-semiconductor junction [12]. In this way one can understand why the current flow initiated in the elastic part of nanoindentation drops down at the instant of pop-in event (figure 3b). Namely, if the mean contact pressure is sufficient to start GaAs-I $\rightarrow$ GaAs-II transformation, the nucleated rocksalt-like phase restores Shottky barrier between small volume of metallic GaAs-II phase and surrounding semiconducting GaAs-I.

4. Conclusion

In summary, the onset of plastic deformation in GaAs crystal witnessed by displacement burst on nanoindentation load-displacement curve that corresponds to sudden halting of the current running through the indenter/GaAs contact is explained in terms of zinc-blende to rocksalt phase transformation. This results contradicts commonly accepted dislocation-based scenario and contributes to our understanding of nanoscale plasticity in III-V semiconductor compounds.

Acknowledgements

The authors acknowledge support from the Academy of Finland (FINNANO project). The calculations were performed at the CSC-IT Center for Science, Finland.

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