Nanoindentation-Induced Deformation of Semiconductors

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A thesis submitted for the degree of Doctor of Philosophy at the Australian National University

ABSTRACT

Mechanical deformation in semiconductor materials is an area of both technological importance and fundamental interest. The influence of mechanical damage on the properties of semiconductors is crucial in the design and fabrication of nanoscale electronic and optoelectronic devices. Semiconductors (particularly silicon) have been traditionally viewed as ideal brittle materials which, under application of local pressure or indentation load, behave elastically until the point of fracture. However, this is not the case in practice, with semiconductors observed to undergo an elastic to plastic transformation at indentation loads well below the threshold for cracking. Based on diamond-anvil isostatic experiments, it has been suggested that such plastic deformation in semiconductors under nanoindentation may be the result of a transformation to a high-pressure (metallic) phase. It has been further suggested that hardness of Group IV and III-V semiconductors should be controlled by this process. However, despite a number of studies addressing the deformation behavior of semiconductors under indentation testing, it is only for Si that a phase transformation has been confirmed, and few details on deformation mechanisms for any of the semiconductors are available. The main reason is that changes in mechanical behavior under indentation loading/unloading have not been supported by detailed microstructural characterization.

Nanoindentation is, in principle, an ideal method for studying mechanical deformation in semiconductors since details of load-unload curves and hardness parameters (particularly using spherical indentation) can be directly correlated with the induced structural changes. In addition, indentation produces technologically-relevant damage, typical of that obtained during semiconductor handling. However, the observation of the complex structural changes induced by nanoindentation has proven to be elusive due to the small, localized damage regions. As a result, it has not been previously possible to examine the deformation microstructures from low-load damage, nor has the evolution of structural changes, which accompany plastic deformation at larger loads, been identified.

The work presented in this thesis has addressed the paucity of information on the structural changes that occur in a range of semiconductors by using a gamut of both in-situ and ex-situ techniques to characterize mechanical deformation. The motivation here has been to identify deformation mechanisms. In this regard spherical indentation used in this study has been favored since, in this case, the stress field is more uniformly distributed under the indenter, and hence analysis is more straightforward. Characterization techniques used include: atomic force microscopy, Raman microspectroscopy, cathodoluminescence (CL) imaging, and cross-section transmission electron microscopy (XTEM). In addition, a novel in-situ electrical characterization technique, developed as a part of this work, has enabled the direct correlation of structural (phase) changes with features in the nanoindentation load-unload curves. In order to overcome the problem of preparing XTEM samples of highly localized regions of indentation-induced mechanical damage, focused-ion-beam milling has been used. The range of semiconductors examined includes both elemental (Si and Ge) and compound (InP, GaAs, GaN and ZnO), with both cubic (Si, Ge, InP and GaAs) and hexagonal (GaN and ZnO) structures.

The results obtained during this study have revealed a rich array of deformation processes across the range of semiconductors examined, including several phase transformations (in Si) and twinning, dislocation slip and cracking depending on loading conditions and the material under study. For the compound semiconductors, the response of the cubic materials (InP and GaAs) to nanoindentation is to plastically deform via the initiation and propagation of (dislocation) slip along the {111} planes. Both XTEM and Raman analyses showed no evidence of phase transformations in InP and GaAs. At higher loads, sub-surface cracking caused by dislocation pile-up was also revealed. In contrast, no cracking was found after nanoindentation loading of the hexagonal materials GaN and ZnO. XTEM of these materials revealed that the prime deformation mechanism in both GaN and ZnO is the nucleation of slip on both the basal and pyramidal planes. Some indication of dislocation pinning was observed on the basal slip planes, and which may lead to a `slip-stick' behavior. Again, no evidence of a phase transformation was obtained in these materials. For

both GaN and ZnO, CL imaging revealed a quenching of near-gap emission by deformation-produced defects. Moreover, both XTEM and CL showed that, in ZnO, defects propagate well beyond the deformed volume under contact. Hence, results of this study have significant implications for the extent of contact-induced damage during fabrication of ZnO-based (opto)electronic devices.

It is interesting to note that phase transformation processes were found to dominate the deformation mechanisms of Si but not of the structurally-similar material, Ge. Instead, XTEM showed that, in Ge, plastic deformation at room temperature occurred predominantly by twinning and dislocation motion. This indicates that the hardness of Ge is not necessarily dominated by a phase transformation, as had previously been thought. Supported by the in-situ electrical characterization technique, the evolution of complex deformation behavior in Si during nanoindentation was studied in detail. On loading, diamond-cubic Si (Si-I) does undergo slip but also transforms to a metallic (Si-II) phase. On unloading, Si-II transforms to a number of less electrically conducting phases of Si. It is suggested that, although crystalline Si-III and Si-XII are the preferred low pressure phases during pressure release, amorphous Si is often obtained during fast unloading rates predominantly as a result of a high kinetic barrier to nucleation of the crystalline phases. Such structural changes have been correlated with fine details of spherical indentation load-unload curves to provide a comprehensive picture of the complex deformation mechanisms in Si.