Chapter 4

Summary

*I*n short, we have demonstrated a systematic study of the nanolithographic and nanomechanical mechanisms/characterizations on semiconductors with the aid of *Scanning Probe Microscopes* (SPMs) and/or *Molecular Dynamics* (MD) simulations. The following conclusions of Chapter 2 and Chapter 3 are drawn.

1.) AFM nanopatterning of GaAs surface

SPM-mediated patterning methods are effective for the creation of nanostructures on surfaces. The approaches described take advantage of the high spatial resolution of SPM based methods and their inherent capabilities for electrical or mechanical modification of surface to allow the precise positioning of nanoscale size features.

AFM nanooxidation is well-established technique for fabricating nanostructures and nanodevices. The proper control of the oxidation reaction, improvement of reproducibility and increasing the precision are meaningful objectives for further evolution of this technique, along with understanding the nanooxidation mechanisms. The nanoscale *p*-GaAs(100) oxide dots, wires and bumps are achieved by employing the AFM-based lithography technique. The main objectives of this study are not only to understand the physical characterizations of semiconductor materials, but also to take the detailed mechanisms of the nanolithography processes.

1.) The purpose of this part is to investigate some of the mechanisms and kinetics of *p*-GaAs(100) surface by AFM tip-induced nanooxidation process, which enhanced by a tip-sample electric field in the present of humidity and its electrochemical characteristics have displayed the importance of the mechanisms of the space charge and the ionic diffusion. First, the growth norm must be the same in both phenomena, since it is limited only by electric-field-stimulated ionic diffusion into the oxide structures. Thus, it is expected that there exists a mechanism to reduce the electric field strength within the oxide dots. For such mechanism, an increase in the H^+ ion concentration near the oxide layer during the anodization processes has been considered [#]. As the anodization time progresses, the H^+ concentration in the oxide grows and becomes significantly. As a result of the screening effect of the H^+ ions, there is a decrease in the electric field within the oxide dots and this may be the reason for lower oxidation. Second, as revealed by AES analysis, it suggests that the incorporation of oxygen into *p*-GaAs(100) surface is enhanced because AFM nanooxidation process results in the formation of anodized oxides.

2.) High humidity (over 60%) promotes the contribution of ionic diffusion through surface water layers, resulting in oxide dots with the “two-storied” shape illustrated in Fig.2-7(a) with broad base and protruding core part are observed in an AFM topographic image. Here, we have attributed this “two-storied” shape dot to the existence of space charge effects and ionic diffusion through the adsorbed water layer.

3.) The AFM-based nanoindentation results indicate that an ISE of nanohardness of the anodized dots and wires which at a threshold point as the indentation depth is of 2nm.

4.) The electrical characterization shows that the electron transports across a GaAs nanooxide dot, which follows the FN-tunneling mechanism over a range of applied anodized voltages.

5.) Taking account of CNT scanning probes as applied to AFM nanooxidation, the height and the aspect ratio of oxide structures can be significantly improved than a conductive tip. Furthermore, application of pulsed voltages was proved to be an efficient method for suppressing the growth of oxide width to further enhanced the aspect ratio by repeatedly breaking the directional transport of OH^- ions in the nanooxidation process. Under DC voltage pulses, the release of H_2O during the neutralization reaction with $H^+ + OH^- \rightarrow H_2O$, which could give rise to the formation of water related defects inside the oxide structures. This could explain the lower density of oxides. In addition, the H^+ accumulation within the oxide could be one of the main reasons of the deviation from Cabrera-Mott kinetics. Nevertheless, this effect can be reduced by the application of AC voltage pulses. The negative part of the voltage pulse decreases the concentration of H^+ ions in the oxide. As a consequence, the oxidation rate is higher for AC voltage pulses. From these results, it is believed that the space charge should be minimized by applying a pulsed bias voltage for improving the aspect ratio of fabricated oxides.

Controlling the lateral growth rate of oxide is a main challenge for the improvement of the fabricating resolution. Our results show that applying pulsed voltage is a feasible method for achieving better resolution with the AFM-based local oxidation technique using CNT probes.

[#] J.A. Dagata, T. Inoue, J. Itoh, and H. Yokoyama, Appl. Phys. Lett. 73 (1998) 271.

2.) Nanoindentation-induced deformation of semiconductors

Nanoindentation has become ubiquitous for the measurement of mechanical properties at ever-decreasing scales of interest. With substantial guidance from atomistic simulations, the onset of plasticity during nanoindentation is now widely believed to be associated with homogeneous dislocation nucleation. Complementary MD simulations and experiments have been carried out to determine the atomistic mechanisms of the nanoindentation process in GaAs. The dislocations formation and motion cause the complex mechanisms of plastic and elastic deformation which is reflected in the dislocation patterns. The following conclusions are obtained:

1.) "Pop-out" and "elbow" events are displayed in unloading curves of Si and Ge during nanoindentation, indicating that the phase transformation.

    For Group III-V semiconductors, "pop-in" events have been observed in the load-displacement curves. Slip, which may also contribution to the "pop-in" observed during contact loading, is shown a major mechanism for plastic deformation in the four semiconductors GaAs, GaN, GaSb and InP.

2.) XTEM and microRaman studies of Si and Ge concluded that phase transformation rather than dislocation slip displayed during loading and, this transformation was responsible for the majority of the observed plastic deformation. For Si, a reasonable explanation for such phase distribution is that the surface layer is less constrained than the deeper region and has no time to rearrange into another crystalline phase from the high pressure phase Si-II during pressure release. Si-I is believed to transform to Si-II almost completely under high pressure induced by indentation and therefore transform to metastable crystalline phases of Si-XII and Si-III upon unloading. In addition, microRaman observations provide additional structural phase to reveal underlying mechanisms of phase transformation.

Also, a metallic phase was observed in Ge from Raman peak at 221cm^{-1}.

No evidence (such as extra Raman bands) was found in III-V compound semiconductors (GaAs&GaN&GaSb&InP) that any pressure-induced phase transformations had displayed, in spite of the materials had undergone severe plastic deformation. Also, XTEM micrographs indicated that the slip bands are aligned {111} planes in GaAs and InP. On the other hand, for GaN, dislocations are predominantly along (0001) basal planes, but can also occur at 60° to surface.

3.) MD simulations of Berkovich indentation normal to single crystal of GaAs have been performed in order to examine how the nanomechanical characterizations can be altered by varying the indentation loads and temperatures. Two main deformation mechanisms have been found, i.e. glide of nucleated dislocation loops and slip underneath the indenter tip.

In the plastic range of the load-displacement curve, the pop-in(s) effect was observed in all MD simulations and was associated with the dislocation nucleation activity beneath the indenter tip. During the process of indentation the dislocation structure comprised of dislocation glide loops on the adjacent {111} slip plane. These dissociated loops, which intersected the surface, were shown to originate from the interstitial character loops emitted along the ⟨110⟩ direction. Based on the local strain diagnostic, the mechanical deformation processes were closely related to the coupling of the dislocation-mediated; plasticity, nucleation and propagation of slip (twinning). The deformation twinning systems observed, occurred at lower temperatures during nanoindentation. In addition, the effect that temperature had on the generation of dislocations was an important aspect to consider for realistic simulations of nanoindentation.